

(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 710 628 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
08.05.1996 Bulletin 1996/19

(51) Int Cl. 6: C03C 13/00

(21) Application number: 95120642.4

(22) Date of filing: 12.01.1994

(84) Designated Contracting States:  
AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL  
PT SE

(30) Priority: 15.01.1993 GB 9300085  
15.01.1993 MX 9300200  
09.07.1993 GB 9314236

(62) Application number of earlier application in  
accordance with Art. 76 EPC: 94904238.6

(71) Applicant: THE MORGAN CRUCIBLE COMPANY  
PLC  
Windsor, Berkshire SL4 1EP (GB)

(72) Inventor: Jubb, Gary Anthony  
Worcestershire DY13 OLS (GB)

(74) Representative: Boff, James Charles et al  
c/o Phillips & Leigh  
7 Staple Inn  
Holborn  
London WC1V 7QF (GB)

### Remarks:

This application was filed on 28 - 12 - 1995 as a  
divisional application to the application mentioned  
under INID code 62.

### (54) Saline soluble inorganic fibres

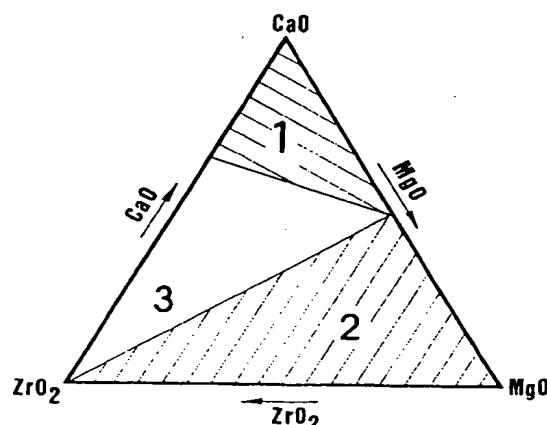
(57) Use is disclosed, at temperatures of 1000°C or  
more for a period of 24 hours, of an inorganic fibre for  
which a vacuum cast preform of the fibre has a shrinkage  
of 3.5% or less when exposed to 1260°C for 24  
hours and comprising CaO, SiO<sub>2</sub>, MgO, optionally ZrO<sub>2</sub>,  
optionally less than 0.75mol% Al<sub>2</sub>O<sub>3</sub>, any incidental impurities  
amounting to less than 2mol% in total, and in  
which

a) the SiO<sub>2</sub> excess (defined as the amount of SiO<sub>2</sub>  
calculated as remaining after the above named constituents  
are crystallised as silicates) exceeds  
21.8mol%;

b) the amount of CaO is greater than the sum of the  
amount of MgO and twice the amount of ZrO<sub>2</sub>; and,

c) the calculated ratio of diopside to wollastonite  
does not lie in the range from more than that of fibre  
E32 to 5.25.

Fig.1



**D**escription

This invention relates to saline soluble, non-metallic, amorphous, inorganic oxide, refractory fibrous materials. The invention particularly relates to glassy fibres having silica as their principal constituent.

Inorganic fibrous materials are well known and widely used for many purposes (e.g. as thermal or acoustic insulation in bulk, mat, or blanket form, as vacuum formed shapes, as vacuum formed boards and papers, and as ropes, yarns or textiles; as a reinforcing fibre for building materials; as a constituent of brake blocks for vehicles). In most of these applications the properties for which inorganic fibrous materials are used require resistance to heat, and often resistance to aggressive chemical environments.

Inorganic fibrous materials can be either glassy or crystalline. Asbestos is an inorganic fibrous material one form of which has been strongly implicated in respiratory disease.

It is still not clear what the causative mechanism is that relates some asbestos with disease but some researchers believe that the mechanism is mechanical and size related. Asbestos of a critical size can pierce cells in the body and so, through long and repeated cell injury, have a bad effect on health. Whether this mechanism is true or not regulatory agencies have indicated a desire to categorise any inorganic fibre product that has a respiratory fraction as hazardous, regardless of whether there is any evidence to support such categorisation. Unfortunately for many of the applications for which inorganic fibres are used, there are no realistic substitutes.

Accordingly there is a demand for inorganic fibres that will pose as little risk as possible (if any) and for which there are objective grounds to believe them safe.

A line of study has proposed that if inorganic fibres were made that were sufficiently soluble in physiological fluids that their residence time in the human body was short; then damage would not occur or at least be minimised. As the risk of asbestos linked disease appears to depend very much on the length of exposure this idea appears reasonable. Asbestos is extremely insoluble.

As intercellular fluid is saline in nature the importance of fibre solubility in saline solution has long been recognised. If fibres are soluble in physiological saline solution then, provided the dissolved components are not toxic, the fibres should be safer than fibres which are not so soluble. The shorter the time a fibre is resident in the body the less damage it can do. H. Förster in *The behaviour of mineral fibres in physiological solutions (Proceedings of 1982 WHO IARC Conference, Copenhagen, Volume 2, pages 27-55(1988))* discussed the behaviour of commercially produced mineral fibres in physiological saline solutions. Fibres of widely varying solubility were discussed.

International Patent Application No. WO87/05007 disclosed that fibres comprising magnesia, silica, calcia and less than 10 wt% alumina are soluble in saline solution. The solubilities of the fibres disclosed were in terms of parts per million of silicon (extracted from the silica containing material of the fibre) present in a saline solution after 5 hours of exposure. The highest value revealed in the examples had a silicon level of 67 ppm. In contrast, and adjusted to the same regime of measurement, the highest level disclosed in the Förster paper was equivalent to approximately 1 ppm. Conversely if the highest value revealed in the International Patent Application was converted to the same measurement regime as the Förster paper it would have an extraction rate of 901.500 mg Si/kg fibre - i.e. some 69 times higher than any of the fibres Förster tested, and the fibres that had the highest extraction rate in the Förster test were glass fibres which had high alkali contents and so would have a low melting point. This is convincingly better performance even taking into account factors such as differences in test solutions and duration of experiment.

International Patent Application No. WO89/12032 disclosed additional fibres soluble in saline solution and discusses some of the constituents that may be present in such fibres. Among such constituents are ZrO<sub>2</sub> and this document claims (among other things) processes using fibres of composition (in weight %): - ZrO<sub>2</sub> 0.06-10%; SiO<sub>2</sub> 35-70%; MgO 0-50%; CaO 0-64.5%. However the patent actually discloses a much more limited range of zirconia containing materials and these are listed in Table 1 below ranked on silica content. None of the disclosed zirconia containing compositions were tested for shrinkage and hence usefulness in high temperature applications: all that these fibres were tested for was ability to withstand a fire test and Table 1 indicates that the results of this test were not very predictable; there does appear to be a trend with silica content but no trend is discernible with zirconia content.

European Patent Application No. 0399320 disclosed glass fibres having a high physiological solubility.

Further patent specifications disclosing selection of fibres for their saline solubility are European 0412878 and 0459897. French 2662687 and 2662688. PCT WO86/04807 and WO90/02713.

Table 1

Test	SiO <sub>2</sub> wt%	CaO wt%	MgO wt%	Al <sub>2</sub> O <sub>3</sub> wt%	ZrO <sub>2</sub> wt%	Fire test Pass/Fail	SiO <sub>2</sub> mol%	CaO mol%	MgO mol%	Al <sub>2</sub> O <sub>3</sub> mol%	ZrO <sub>2</sub> mol%
174	63.5	35.55	0.33	0.88	0.21	P	61.83	37.08	0.48	0.5	0.1

Continuation of the Table on the next page

Table 1 (continued)

Test	SiO <sub>2</sub> wt%	CaO wt%	MgO wt%	Al <sub>2</sub> O <sub>3</sub> wt%	ZrO <sub>2</sub> wt%	Fire test Pass/Fail	SiO <sub>2</sub> mol%	CaO mol%	MgO mol%	Al <sub>2</sub> O <sub>3</sub> mol%	ZrO <sub>2</sub> mol%
178	60	38.3	0.48	0.36	0.54	-	58.7	40.14	0.7	0.21	0.26
177	59.7	38.7	0.46	0.34	0.50	-	58.36	40.53	0.67	0.20	0.24
176	59.5	39.1	0.42	0.31	0.42	-	58.1	40.91	0.61	0.18	0.2
182a	59.4	34.9	2.06	0.38	2.31	P	58.69	36.94	3.03	0.22	1.11
181	59.2	36.6	1.13	0.32	0.83	P	58.8	38.94	1.67	0.19	0.4
179	59.2	37	0.98	0.35	0.58	P	58.74	39.33	1.45	0.2	0.28
175	59.2	39.1	0.41	0.33	0.4	P	57.99	41.03	0.6	0.19	0.19
183	59.05	34.84	3.08	0.3	2.65	P	57.65	36.44	4.48	0.17	1.26
186	59.05	36.94	2.57	0.38	3.27	P	56.63	37.95	3.67	0.21	1.53
191	58.6	33.5	2.72	0.58	3.67	P	58.21	35.65	4.03	0.34	1.78
192	58.4	33.2	2.59	0.65	3.69	P	58.39	35.56	3.86	0.38	1.8
189	58.19	35.39	3.26	0.39	3.36	-	56.59	36.87	4.73	0.22	1.59
184	57.96	35.17	3.55	0.42	3.11	F	56.44	36.69	5.15	0.24	1.48
190	57.86	35.66	3.22	0.36	3.37	F	56.33	37.19	4.67	0.21	1.6
185	57.8	34.4	3.74	0.56	3.12	F	56.62	36.1	5.46	0.32	1.49
188	57.7	36	3	0.2	3.3	P	56.31	37.64	4.36	0.12	1.57
187	56.88	36.45	4	0.32	3.3	-	54.86	37.66	5.75	0.18	1.55
193	56.65	31.9	3.35	3.35	4.5	F	56.66	34.18	4.99	1.97	2.19
180	54.3	32.75	10.2	1.29	0.58	F	51.41	33.22	14.39	0.72	0.27
182	46.85	29.2	20.6	2.03	0.84	F	42.42	28.33	27.8	1.08	0.37

The refractoriness of the fibres disclosed in these various prior art documents varies considerably. The maximum service temperature of any of the above mentioned fibres (when used as refractory insulation) is up to 815°C (1500°F).

Among saline soluble commercial fibres usable at temperatures higher than 815°C are SUPERWOOL™ a fibre manufactured by The Morgan Crucible Company plc and which has a maximum use temperature of 1050°C and a composition of SiO<sub>2</sub> 65wt%; CaO 29wt%; MgO 5wt%; Al<sub>2</sub>O<sub>3</sub> 1wt%. A similar fibre is INSULFRAX™ a fibre made by Carborundum Company which has a continuous use limit of 1000°C (1832°F) and which melts at 1260°C (2300°F). This has a composition of SiO<sub>2</sub> 65w%; CaO 31.1wt%; MgO 3.2wt%; Al<sub>2</sub>O<sub>3</sub> 0.3wt% and Fe<sub>2</sub>O<sub>3</sub> 0.3wt%.

Use of ZrO<sub>2</sub> as a constituent in aluminosilicate fibres to provide high temperature resistance is known (see European 0144349). However it is by no means apparent that this effect is transferable to saline soluble fibres and the disclosure of International Patent Application No. WO89/12032 discussed above would tend to suggest that it is not.

The applicant's earlier International Patent Application WO93/15028 (from which this application claims priority) disclosed saline soluble fibres usable at temperatures in excess of 1000°C but gave no indication that fibres could be used at still higher temperatures. The applicants have found that some of the fibres disclosed in WO93/15028 (e.g. fibre A2-13 from Table 9 of WO93/15028) are in fact usable at temperatures of up to 1260°C and even higher. In general the applicants have found that fibres of specified compositions (including zirconia containing fibres) are usable at temperatures up to and beyond 1260°C. The applicants have realised that failure of fibres at high temperature occurs primarily upon devitrification of the fibre; if on devitrification insufficient silica is left the fibres will fail through having a shrinkage of greater than 3.5%. Accordingly the applicants have looked to what materials are formed on devitrification.

In the following where reference is made to a saline soluble fibre this is to be taken as meaning a fibre having a total solubility of greater than 10ppm in saline solution as measured by the method described below, and preferably having much higher solubility.

Figure 1 shows a three axis composition diagram for the constituents CaO, MgO, and ZrO<sub>2</sub>; this diagram omits all other constituents so that the sum of CaO, MgO, and ZrO<sub>2</sub> at all points is 100%. Silica is in excess at all points as described below.

For fibres where  $\text{CaO} > \text{MgO} + 2\text{ZrO}_2$  all of the  $\text{MgO}$  is bound as  $\text{CaO}.\text{MgO}.2\text{SiO}_2$ ; all of the  $\text{ZrO}_2$  is bound as  $2\text{CaO}.\text{ZrO}_2.4\text{SiO}_2$ ; and any excess  $\text{CaO}$  is bound as  $\text{CaSiO}_3$ . These fibres lie in region 1 of Figure 1 and in the following are referred to as excess  $\text{CaO}$  fibres.

For fibres where  $\text{MgO} > \text{CaO}$  all of the  $\text{CaO}$  is bound as  $\text{CaO}.\text{MgO}.2\text{SiO}_2$ ; all of the  $\text{ZrO}_2$  is bound as  $\text{ZrO}_2.\text{SiO}_2$ ; and the excess  $\text{MgO}$  is bound as  $\text{MgO}.\text{SiO}_2$ . These fibres lie in region 2 of Figure 1 and in the following are referred to as excess  $\text{MgO}$  fibres.

For the fibres in region 3 of Figure 1 where  $\text{CaO} > \text{MgO}$  and  $\text{CaO} < \text{MgO} - 2\text{ZrO}_2$ , all of the  $\text{MgO}$  is bound as  $\text{CaO}.\text{MgO}.2\text{SiO}_2$ ; the rest of the  $\text{CaO}$  is bound as  $2\text{CaO}.\text{ZrO}_2.4\text{SiO}_2$ ; and the excess  $\text{ZrO}_2$  is bound as  $\text{ZrO}_2.\text{SiO}_2$ . These fibres are referred to in the following as excess  $\text{ZrO}_2$  fibres.

The applicants have defined a term "SiO<sub>2</sub> excess" which indicates the amount of silica left once the above mentioned constituents ( $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{ZrO}_2$ ) have crystallised. The value of SiO<sub>2</sub> excess is calculated by subtracting from the total quantity of silica present that amount that should crystallise as silicates with the other constituents CaO, MgO, and ZrO<sub>2</sub> assuming all of the CaO, MgO, and ZrO<sub>2</sub> crystallise as the materials mentioned above. In most of the compositions studied alumina is present to some extent and so the applicants also assume that alumina crystallises as Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> and to calculate SiO<sub>2</sub> excess this quantity is subtracted also. Only the above named constituents are used in calculating the SiO<sub>2</sub> excess as other chemical constituents are present in only small amounts. For other chemical constituents similar considerations apply. It has been found by the applicants that when the SiO<sub>2</sub> excess is greater than 21.8mol% the fibres tend to have a resistance to temperature of up to 1260°C.

The applicants have found that for the excess CaO compositions the situation is complicated by a eutectic formed between the two crystalline materials diopside ( $\text{CaO}.\text{MgO}.2\text{SiO}_2$ ) and wollastonite ( $\text{CaSiO}_3$ ) that has a damaging effect on high temperature resistance. Thus the present invention excludes those excess CaO compositions that have a calculated diopside to wollastonite ratio in the range 1.8 to 5.25.

The physical basis for the importance of SiO<sub>2</sub> excess may be that it indicates how much silica is left to maintain a glassy phase on crystallisation of the other constituents as silicate materials. Further, the silicate materials that form on devitrification may become liquid or flow at 1260°C so causing shrinkage.

The quantity of potentially fluxing constituents such as alkali metals and other incidental impurities (e.g. iron oxides) should be kept low.

Accordingly the present invention provides a refractory fibre for which a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours and comprising CaO, SiO<sub>2</sub>, MgO, optionally ZrO<sub>2</sub> and/or less than 0.75mol% Al<sub>2</sub>O<sub>3</sub>, any incidental unurities amounting to less than 2mol% in total, and in which the SiO<sub>2</sub> excess (defined as the amount of SiO<sub>2</sub> calculated as remaining after the above named constituents are crystallised as silicates) exceeds 21.8mol%, with the proviso that, if the amount of CaO is greater than the sum of the amount of MgO and twice the amount of ZrO<sub>2</sub> the calculated ratio of diopside to wollastonite does not lie in the range 1.8 to 5.25.

The applicants have also found that for those fibres that have a satisfactory shrinkage at 1260°C the saline solubility of the fibres produced appears to increase with increasing amount of MgO present whereas ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are detrimental to solubility. The invention therefore also provides preferred saline soluble fibres of the composition specified above and in which the MgO excess [defined as  $\text{MgO} - (\text{ZrO}_2 + \text{Al}_2\text{O}_3)$ ] is greater than 10mol%, such fibres tending to have a total solubility of MgO + SiO<sub>2</sub> - CaO of greater than 50ppm (see below for measurement details). More preferably the MgO excess is greater than 11.2mol% such fibres tending to have extremely high solubility of about 100ppm or more. Yet more advantageously, so far as solubility is concerned, the MgO excess is nearer than 15.25mol%: all of the fibres measured having an MgO excess greater than 15.25mol% had solubilities in excess of 100ppm.

As a consequence of inventing these fibres the invention also provides a saline soluble fibre characterised in that a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours.

The applicants have investigated, for then saline solubility and refractoriness, a range of compositions based on CaO/MgO/SiO<sub>2</sub> fibres with additional constituents Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>. These fibres were formed by blowing the molten constituents from a melt stream in a conventional manner but the invention is not limited to blown fibres and also encompasses fibres formed by spinning or any other means.

Tables 2 & 3 show the results of these tests. Table 2 indicates for each the linear shrinkages at 800, 1000, 1200, and 1260°C (not all samples measured at every temperature); weight percent composition; mole percent composition (based on the constituents CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>); SiO<sub>2</sub> excess (as defined above) and, for the CaO excess fibres, the calculated diopside to wollastonite ratio. Table 3 indicates for each the weight percent composition; mole percent composition (based on the constituents CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>); solubilities of various constituents; and MgO excess (as defined above). Each sample that has a satisfactory shrinkage of 3.5% or less at 1260°C is indicated by a composition shown in bold. Those compositions that fail to meet the shrinkage criterion are indicated in italics. Other compositions are shown falling within the described ranges but for which the high temperature shrinkage was not measured: these compositions are indicated in plain text. Those compositions where a fibre could not be made or where the fibre was of too poor a quality for the solubility to be measured are indicated with X's.

A pattern emerges which is described below with reference to Table 2.

The fibres above and including line A all have a  $\text{SiO}_2$  excess of less than 21.8mol% and all (where measured) fail the shrinkage criterion that a vacuum cast preform of the fibre has a shrinkage of less than 3.5% when exposed to 1260°C for 24 hours.

The fibres above and including line B and below line A all have a  $\text{TiO}_2$  content of greater than 1.25mol% and all fail the shrinkage criterion.

The fibres above and including line C and below line B all have a  $\text{Al}_2\text{O}_3$  content of greater than 0.75mol% and all fail the shrinkage criterion.

The fibres below line C are grouped according to their relative amounts of  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{ZrO}_2$  (i.e. as to their positions in Figure 1)

The fibres above and including line D and below line C are the excess  $\text{MgO}$  fibres (region 2 of Figure 1) and are sorted on  $\text{SiO}_2$  excess.

The fibres above and including line E and below line D are the excess  $\text{ZrO}_2$  fibres (region 3 of Figure 1) and are sorted on  $\text{SiO}_2$  excess.

The fibres below line E are the excess  $\text{CaO}$  fibres and are sorted on the diopside to wollastonite ratio.

The fibres above and including line F and below line E are excess  $\text{CaO}$  fibre for which the diopside to wollastonite ratio is greater than 5.25.

The fibres above and including line G and below line F are excess  $\text{CaO}$  fibre for which the diopside to wollastonite ratio is less than 5.25 but greater than 1.8.

The fibres below line G are excess  $\text{CaO}$  fibre for which the diopside to wollastonite ratio is less than 1.8.

Looking first to the excess  $\text{MgO}$  fibres most pass the shrinkage criterion at 1260°C (where tested). B7D, BZ-440C, 37C, and BZ-4150C all contain relatively high levels of  $\text{Fe}_2\text{O}_3$  (1.1wt% for B7D and 0.6wt% for the others).

D3 and D8 contain relatively high levels (0.71mol% and 0.74 mol%) of  $\text{TiO}_2$  and it may be that this, in combination with other impurities, has led to failure. It should be noted that D9 has 0.65mol%  $\text{TiO}_2$  and has a satisfactory shrinkage.

BZ-440A, B7A, BZ-4150A, and BZ-560B have varying amounts of  $\text{Na}_2\text{O}$  present (0.3-1.0wt%) and this may contribute to their failure.

BZ-4150B has a  $\text{Al}_2\text{O}_3$  content of 0.64mol% and fails the shrinkage criterion. This should be contrasted with BZ-4150 which has a similar composition but with only 0.06mol%  $\text{Al}_2\text{O}_3$  and which passes the shrinkage criterion. In further contrast BZ-560E has an alumina content of 0.62mol% and passes the shrinkage criterion: this composition has a much higher  $\text{ZrO}_2$  content than BZ-4150B and the applicant believe that the presence of  $\text{ZrO}_2$  allows the fibres to tolerate much higher levels of impurities than would otherwise be the case.

D3 only just fails with a shrinkage of 3.8% and B19 only has a shrinkage of 3.6% at 1260°C and both may in fact be errors in measurement.

Looking next to the excess  $\text{ZrO}_2$  fibres all apart from BZ-407, BZ-429 and BZ-430 pass the shrinkage criteria at 1260°C (where tested). These results may indicate that the incidental impurities (shown as "Others" in Table 2) are having an effect as BZ-429 and BZ-430 show high levels of impurities (1.1 and 0.9 wt% respectively) that on analysis included 0.4 and 0.3 wt% respectively of  $\text{Na}_2\text{O}$ . BZ-430 only just failed the shrinkage criterion (3.7% shrinkage) and this may be due to error in measurement.

Turning now to the excess  $\text{CaO}$  fibres the pattern is clear but not exact. Fibres that have a diopside to wollastonite ratio of between 5.25 and 1.8 fail the shrinkage criterion. Those with a diopside to wollastonite ratio outside this range tend to pass. The fit is not exact and the fibres that fail to meet the shrinkage criterion are the following:

Among the excess  $\text{CaO}$  fibres with a diopside to wollastonite ratio in excess of 5.25 those that fail the shrinkage criterion include BZ-418, and BZ-29 which have low enough shrinkages that they may be the result of experimental error and these fibres may in fact have a satisfactory shrinkage.

BZ-421, B13, BZ-422, BZ-417, and BZ-416 also fail and although initial indicators were that this had something to do with the level of  $\text{CaO}$  this now appears to be incorrect. The failure to meet the shrinkage criterion may be due to the presence of fluxing constituents or otherwise. A possible reason for failure of BZ-29 and BZ-421 may be their high  $\text{Al}_2\text{O}_3$  content (0.55 and 0.51 mol% respectively) acting alone or in combination with impurities.

For the excess  $\text{CaO}$  fibres having a diopside to wollastonite ratio of less than 1.8 the only fibre proven to fail was fibre E24 which although passing a 1260°C test failed a 1200°C test. This result may have been due to experimental error, fluxing components, or otherwise.

Table 3 shows the solubilities of the fibres shown in Table 2 but ranked on  $\text{MgO}$  excess. Although by no means exact it can be seen that there is a trend in total solubility that closely follows  $\text{MgO}$  excess.

In any event the trend appears to be that excess  $\text{CaO}$  fibres perform poorly (perhaps due to the formation of  $\text{CaSiO}_3$  which is not formed in excess  $\text{MgO}$  or excess  $\text{ZrO}_2$  fibres) whereas excess  $\text{MgO}$  and excess  $\text{ZrO}_2$  fibres perform better. Taken to the extreme this would indicate that a high  $\text{MgO}$ , low  $\text{CaO}$ , low  $\text{ZrO}_2$ , low  $\text{Al}_2\text{O}_3$  fibre would have very high solubility and low shrinkage. However the applicant's experience is that such fibres are difficult to form (see Compositions A2-33, (A2-32,A2-28). Equally fibres that are too high in  $\text{SiO}_2$  are difficult or impossible to form. The exact boundaries are difficult to ascertain and this invention only encompasses fibres that meet the above stated shrinkage

requirements.

The applicants have tested some fibres to higher temperatures.

Fibres BZ-400, BZ-440, BZ-48, and BZ-54 were tested to 1350°C and all failed having shrinkages in excess of 20%.

Fibres BZ-400, BZ-36, BZ-46, and BZ-61 were tested to 1300°C and had shrinkages, respectively, of 6.2%, 17.9%,

19.6%, and 3.1%. BZ-61 is in the excess MgO region and the applicants surmise (since  $2\text{CaO} \cdot \text{ZrO}_2 \cdot 4\text{SiO}_2$  is not formed in this region) that it is this constituent that causes failure at 1300°C.

The fact that fibre shrinkage is so dependent on temperature (the fibres failing over such short temperature ranges as 1260°C to 1300°C and 1300°C to 1350°C) is a clue as to how experimental errors may arise. In a typical experimental furnace running at a nominal 1260°C temperatures can easily range from 1250°C to 1270°C both physically (from front to back or centre to wall of furnace) and in time (as the furnace controller supplies or stops current to the furnace). A 20°C temperature difference could easily move a sample from a temperature at which it passes to one at which it fails the 3.5% shrinkage criterion. As mentioned above this may explain the shrinkages of just over 3.5% found for compositions B19, D3, BZ-430, BZ-418 and BZ-29.

During the shrinkage tests some of the sample preforms used were also inspected to ascertain whether they reacted adversely with the ceramic boards (alumina or mullite boards) on which they rested during the test. It was found that the excess CaO fibres with a diopside to wollastonite ratio of less than 1.8 reacted particularly badly with mullite boards and further that due to acicular crystal growth the fibres tended to lose strength.

The following describes in detail the methods used to measure shrinkage and solubility.

Shrinkage was measured by proposed ISO standard ISO/TC33/SC2/N220 equivalent to British Standard BS 1920, part 6, 1986 with some modifications to account for small sample size. The method in summary comprises the manufacture of vacuum cast preforms, using 75g of fibre in 500cm<sup>3</sup> of 0.2% starch solution, into a 120 x 65mm tool. Platinum pins (approximately 0.1-0.3mm diameter) were placed 100 x 45mm apart in the 4 corners. The longest lengths (L1 & L2) and the diagonals (L3 & L4) were measured to an accuracy of  $\pm 5\mu\text{m}$  using a travelling microscope. The samples were placed in a furnace and ramped to a temperature 50°C below the test temperature at 400°C/hour and ramped at 120°C/hour for the last 50°C to test temperature and left for 24 hours. The shrinkage values are given as an average of the 4 measurements.

It should be noted that although this is a standard way of measuring shrinkage of fibre it has an inherent variability in that the finished density of the preform may vary depending on casting conditions. Further it should be noted that fibre blanket will usually have a higher shrinkage than a preform made of the same fibre. Accordingly the 3.5% figure mentioned in this specification is likely to translate as a higher shrinkage in finished blanket.

The applicants have looked to the various incidental impurities that can occur in inorganic oxide refractory fibres (e.g. alkali oxides and iron oxide) and have found that the impurity levels that can be tolerated vary according to the proportions of the main constituents of the fibre. Fibres containing high levels of ZrO<sub>2</sub> for example can tolerate higher levels of Na<sub>2</sub>O or Fe<sub>2</sub>O<sub>3</sub> than fibres with low levels of ZrO<sub>2</sub>. Accordingly the applicants propose a maximum level of incidental impurities of 2mol%, the maximum level that will be tolerable will however vary as mentioned above.

Solubility was measured by the following method.

The fibre was first chopped - 2.5 g of fibre (deshotted by hand) was liquidised with 250 cm<sup>3</sup> of distilled water in a domestic Moulinex (Trade Mark) food blender for 20 seconds. The suspension was then transferred to a 500 cm<sup>3</sup> plastic beaker and allowed to settle after which as much liquid as possible was decanted and the remaining liquid removed by drying in an oven at 110°C.

The solubility test apparatus comprised a shaking incubator water bath, and the test solution had the following composition:-

Compound	Name	Grains
NaCl	Sodium chloride	6.780
NH <sub>4</sub> Cl	Ammonium chloride	0.540
NaHCO <sub>3</sub>	Sodium bicarbonate	2.270
Na <sub>2</sub> HPO <sub>4</sub> .H <sub>2</sub> O	Disodium hydrogen phosphate	0.170
Na <sub>2</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> .2H <sub>2</sub> O	Sodium citrate dihydrate	0.060
H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> H	Glycine	0.450
H <sub>2</sub> SO <sub>4</sub> s.g. 1.84	Sulphuric acid	0.050

The above materials were diluted to 1 litre with distilled water to form a physiological-like saline solution.

0.500 grams  $\pm 0.0003$  grams of chopped fibre was weighed into a plastic centrifuge tube and 25 cm<sup>3</sup> of the above saline solution added. The fibre and saline solution was shaken well and inserted into the shaking incubator water bath maintained at body temperature (37°C  $\pm 1^\circ\text{C}$ ). The shaker speed was set at 20 cycles/minute.

## EP 0 710 628 A2

After the desired period (usually 5 hours or 24 hours) the centrifuge tube was removed and centrifuged at 4500 revs/minute for approximately 5 minutes. Supernatant liquid was then drawn off using a syringe and hypodermic needle. The needle was then removed from the syringe, air expelled from the syringe, and the liquid passed through a filter (0.45 micron cellulose nitrate membrane filter paper [WCN type from Whatman Labsales Limited]) into a clean plastic bottle. The liquid was then analysed by atomic absorption using a Thermo Jarrell Ash Smith - Hiefe II machine.

The operating conditions were as follows using a nitrous oxide and acetylene flame:-

ELEMENT	WAVELENGTH (nm)	BRAND WIDTH	CURRENT (mA)	FLAME
Al	309.3	1.0	8	Fuel Rich
SiO <sub>2</sub>	251.6	0.3	12	Fuel Rich
CaO	422.7	1.0	7	Fuel Lean
MgO	285.2	1.0	3	Fuel Lean

The procedure and standards adopted for determining the above elements were as set out below.

SiO<sub>2</sub> can be determined without dilution up to 250 ppm concentration (1 ppm 1mg/Litre). Above this concentration an appropriate dilution was made volumetrically. A 0.1% KCl solution (0.1g in 100 cm<sup>3</sup>) was added to the final dilution to prevent ionic interference. NB If glass apparatus is used, prompt analysis is necessary.

From a stock solution of 1000 ppm pure ignited silica (99.999%) (fused with Na<sub>2</sub>CO<sub>3</sub> at 1200°C for 20 minutes in a platinum crucible (0.2500g SiO<sub>2</sub>/2g Na<sub>2</sub>CO<sub>3</sub>) and dissolved in dilute hydrochloric acid (4 molar) made up to 250cm<sup>3</sup> with distilled water in a plastic volumetric flask) the following standards were produced:-

STANDARD (ppm SiO <sub>2</sub> )	STOCK SOLUTION (cm <sup>3</sup> )
10.0	1.0
20.0	2.0
30.0	3.0
50.0	5.0
100.0	10.0
250.0	25.0

Add 0.1% KCl to each standard before making to 100cm<sup>3</sup>.

Aluminium may be measured directly from the sample without dilution. Standards of 1.0, 5.0 and 10.0 ppm Al may be used. For calibration readings are multiplied by 1.8895 to convert from Al to Al<sub>2</sub>O<sub>3</sub>.

A standard Al atomic absorption solution (e.g. BDH 1000 ppm Al) was bought and diluted using an accurate pipette to the desired concentration. 0.1% KCl was added to prevent ionic interference.

Calcium may require dilutions on the sample before determination can be carried out (i.e. x 10 and x 20 dilutions). Dilutions must contain 0.1% KCl.

A standard Ca atomic absorption solution (e.g. BDH 1000 ppm Ca) was diluted with distilled water and an accurate pipette to give standards of 0.5, 4.0 and 10.0 ppm. 0.1% KCl is added to prevent ionic interference. To convert readings obtained from Ca to CaO a factor of 1.4 was used.

Magnesium may require dilutions on the sample before determinations can be made (i.e. x 10 and x 20). Add 0.1% KCl to each dilution. To convert Mg to MgO multiply by 1.658.

A standard Mg atomic absorption solution (e.g. BDH 1000 ppm Mg) was diluted with distilled water and an accurate pipette to give standards of 0.5, 1.0 and 10.0 ppm Mg. 0.1% KCl was added to prevent ionic interference.

All stock solutions were stored in plastic bottles.

The above has discussed resistance to shrinkage of preforms exposed to 1260°C for 24 hours. This is an indication of the maximum use temperature of a fibre. In practice fibres are quoted for a maximum continuous use temperature and a higher maximum exposure temperature. It is usual in industry when selecting a fibre for use at a given temperature to choose a fibre having a higher continuous use temperature than that nominally required for the intended use. This is so that any accidental increase in temperature does not damage the fibres. It is quite usual for a margin of 100 to 150°C to be given. Accordingly this invention extends to use of the claimed fibres at elevated temperatures (i.e. at temperatures where the refractoriness of fibres is important) and not just to use at 1260°C.

In selecting a fibre a balance has to be struck between refractoriness of the fibre and saline solubility of the fibre. For example the applicants have found the best high solubility fibre (total solubility greater than 100ppm) is probably composition B7 as that has a shrinkage of 2.7% at 1260°C. In contrast the best refractory fibre is probably BZ-560 which has a shrinkage of only 2.1% at 1260°C but has a total solubility of only 27ppm. Although there are other fibres

**EP 0 710 628 A2**

with a lower shrinkage this fibre also has the property of retaining in large part its resilience on firing to 1260°C - many of the fibres become rigid after firing due to crystallisation and sintering. It appears that high levels of ZrO<sub>2</sub> help to overcome this (BZ-560 has 7.64mol% ZrO<sub>2</sub>) but at the same time reduce solubility.

5 It will be evident from the above that incidental impurity levels are preferably kept as low as possible. The applicants surmise that as the various crystalline materials crystallise from the fibres impurities migrate to the grain boundaries and concentrate there. Thus a small impurity can have a very large effect.

10

15

20

25

30

35

40

45

50

55

5

10

15

20

25

30

35

40

45

50

55

## EP 0 710 628 A2

Table 2 (sheet 1)

Comp.	Shrinkage				Composition				Wt%				Composition				mol%				SiO <sub>2</sub>		Comments			
	800°C	1000°C	1200°C	1260°C	CaO	MgO	ZnO	TiO <sub>2</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Others	Cat	MgO	ZnO	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	SiO <sub>2</sub> excess	Dioptase	Wollastonite	Ratio				
CAS10	0.6	10.7	10.3	10.3	50.3	24.6	23.6	38.82	15.67	14.74	4.87	51.51	25.51	-18.98												
BZ-14	36.6	10.7	27.1	9.9	10	0.4	0.7	51.2	0.7	29.00	14.74	51.15	51.15	-2.57												
C-4S-4	0.3	31.3	33.7	19.7	0.4	0.2	36.6	42.5	0.5	24.58	0.69	0.11	25.12	49.30	-1.12											
BZ-13	1.1	1.1	32	5.1	10	0.5	50.9	0.7	31.00	7.76	4.98	0.30	51.96	1.03												
71	51.7	21.04	19.66	0.2	54.68	23.44	26.67	0.11	59.77	0.45																
765	34.2	3.9	35.07	2.12	57.78	3.62	45.26	1.08	50.04	0.07																
BZ-24	26.9	22.2	9.9	1.5	0.3	51.2	0.8	24.46	15.18	7.52	0.08	52.86	0.68													
BZ-23	6.4	10.2	19.1	26.5	5	14.9	0.5	51.4	0.8	29.95	7.66	0.31	54.22	0.77												
734	39.3	26.62	17.05	0.05	1	56.58	25.66	22.87	0.02	0.53	50.92	1.81														
973	34.9	24.45	16.81	0.05	0.5	56.18	24.31	23.25	0.02	0.27	52.14	4.20														
971	41.7	23.92	17.36	0.05	0.74	56.82	23.56	23.79	0.02	0.40	52.23	4.47														
BZ-27	2.6	10.1	19	23.8	5.1	11.6	0.4	55.9	0	27.00	8.05	7.64	0.35	57.07	6.49											
BZ-0	27.8	44.7	27.1	10	5	0.4	56	0.6	28.29	14.53	2.38	0.33	54.58	6.77												
708	5.7	1.1	42.79	0.77			55.22	14.83	1.12					54.03	8.03											
12-19	4.7	18.48	19.74	0.54			58.71	18.29	27.18					54.24	8.47											
12-18	56.2	26.29	13.01	0.66			56.96	26.85	18.48					54.30	8.59											
BZ-28	5.9	19.4	9.9	15.1	0.3	54.5	0.6	21.30	15.12	7.55	0.18	55.85	8.62													
BZ-3	34.7	36.07	14.44	1.46	0.38	53.99	37.77	6.47	0.70	0.33	54.73	8.76														
BZ-9	31.5	31.8	5.1	0.6	0.6	56	33.95	7.43	2.48	0.33	55.80	9.12														
BZ-26	26.6	30.5	9.44	0.62	0.62	56.98	31.39	13.52	0.35	0.37	54.74	9.48														
BZ-21	3.1	11.9	16.8	22.3	5	15.2	0.3	56.4	0.7	25.06	7.82	7.77	0.19	59.16	10.55											
12-23	10.7	18.9	18.59	18.78	0.05	0.48	60.2	18.37	25.82	0.02	0.26	55.53	11.06													
BZ-12	7.4	14.8	21.3	9.7	10.2	0.3	57.8	0.8	22.77	14.42	4.96	0.18	57.67	11.17												
12-24	12.3	13.62	22.74	0.08	0.31	61.38	13.25	30.79	0.04	0.17	55.76	11.51														
932	12.8	21.6	15.65	0.11	1.5	59.85	21.58	21.75	0.05	0.82	55.80	11.60														
714	1.2	0.7	32	8.27			59.05	32.45	11.67					55.89	11.78											
BZ-11	6.6	17.2	22	26.2	5	10.2	0.4	57.4	0.8	28.60	7.59	5.07	0.24	58.49	11.92											
660	24.7	34.65	4.83	1.15	1.15	57.74	36.13	7.01					56.20	12.40												
712	3.4	35.39	4.61	0.06	0.91	57.54	37.04	6.71					56.21	12.43												
Bz-20	30.9	32.7	6.07	0.91	0.91	57.57	34.28	8.85	0.12	0.32	56.34	12.68														
42-25	6.1	10.99	24.16	0.07	0.33	62.36	10.66	32.64	0.03	0.48	56.48	12.97														
BZ-23	2.2	3.9	11.6	20.7	3.2	15.3	0.3	57.3	0.7	23.33	8.16	7.96	0.19	60.34	13.09											
694	1.9	1.6	33.1	6.02	0.17	0.27	58.39	34.41	8.71	0.08	0.15	56.65	13.23													
A2-11	1.1	1.8	24.28	13.24	0.08	0.25	60.32	24.48	18.57	0.04	0.14	56.77	13.51													
BZ-27	30.3	36.62	2.43	0.08	0.73	57.38	38.96	3.60	0.04	0.43	56.98	13.92														
692	2.1	34.34	5.44	0.17	0.13	59.82	35.08	7.73	0.08	0.07	57.04	14.00														
B8	2.6	6.9	18.8	1.9	0.3	0.2	63	0.2	18.30	24.24	0.13	0.11	57.23	14.46												
BZ-22	7.6	20.7	21.3	17.1	9.8	15.2	0.4	56.7	0.7	18.83	15.02	7.62	0.24	58.29	14.67											
E21	1.4	3.4	5.6	39.1	0.7	0.6	58.2	0.5	41.28	1.03	0.35	0.27	57.35	14.70												
B3-25	2.3	28.15	9.22				59.51	0.48	59.51	29.08	13.25	0.27	57.40	14.80												

## EP 0 710 628 A2

5

10

15

20

25

30

35

40

45

50

55

Table 2 .... (sheet 2)

Compl	80MgC	10MgC	12MgC	12MgC	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	MgO	ZnO	mol%	SiO <sub>2</sub>	SiO <sub>2</sub>	SiO <sub>2</sub>	Diposite	Wollastonite	Comments	
	(at)	(at)	(at)	(at)					(at)	(at)								
586	1.6	1.9	2.5	3.9	35.03	0.13	0.13	58.65	36.77	5.69	0.08	57.46	14.92					
A2-14	1.8	2.5	3.3	5.8	25.3	0.16	0.28	60.74	25.70	16.48	0.07	57.59	15.11					
12-35	7.1	7.3	0.3	1.4	19.78	1.51	0.47	64.72	8.56	33.37	0.15	57.71	15.41					
924	3.1	0.3	0.3	0.3	30.91	6.15	0.24	58.81	32.68	9.05	0.12	57.84	15.68					
696	1.4	1.4	1.3	2.9	20.92	15.22	0.2	62.6	20.79	21.04	0.11	58.04	15.96					
757	2.9	1.3	3.4	3.9	6.63	26.2	0.8	64.85	6.37	33.01	0.35	58.06	16.13					
12-34	3.9	3.4	1	2.3	16.55	1.8	0.05	63.56	16.37	24.76	0.02	58.15	16.29					
A2-12	2.3	1	2.3	1.4	20.9	4.9	1.32	59.5	0.7	23.37	7.62	6.72	0.18	58.67	17.34			
BZ-19	2.5	1.4	1.6	2.7	16.06	18.21	0.4	63.68	15.89	25.07	0.22	58.82	17.64					
A2-30	1.6	1.1	1.1	1.1	23.37	11.98	0.23	61.98	23.79	16.97	0.11	58.89	17.68					
A2-7	1.7	2.2	5	1x1	17.1	0.7	0.2	64.4	0.2	17.72	23.29	0.04	0.17	58.84	17.69			
B9	3.3	3.2	3.2	3.2	13.74	19.98	0.13	64.16	13.51	27.34	0.06	58.90	17.81					
A2-21	1.2	1.2	1.2	1.2	20.3	9.8	0.2	61.6	0.4	21.42	14.39	3.41	0.12	60.67	17.93			
BZ-41	4.2	7.7	1.7	1.7	19.6	9.7	0.2	60.8	0.6	20.93	14.41	3.94	0.12	60.60	17.95			
BZ-427	3.7	9.6	0.5	0.5	32.56	3.8	0.82	60.11	3.43	5.58	0.39	59.21	18.02					
B3-1	0.5	1.7	2.5	3.2	32.27	3.99	0.09	61.32	3.39	5.84	0.04	59.19	18.34					
B3-1A	1.7	2.5	1.2	1.2	18.9	5	15.2	59	0.7	21.47	7.90	7.86	0.19	62.57	18.36			
BZ-47	1.2	1.04	3.49	2.5	2.5	0.49	0.76	60.28	36.35	3.67	0.24	59.31	18.38					
B3-9	1.7	1.6	7.7	7.7	21.7	9.6	0.5	61.9	0.5	22.73	13.99	2.48	0.29	60.52	18.55			
BZ-2	1.7	3.7	1.7	1.7	19.9	15.1	0.7	64.2	0.4	19.71	20.80	0.05	0.11	59.34	18.68			
B5	1.4	1.8	6	5.6	37.1	0.7	0.6	60.2	0.5	39.20	1.03	0.03	0.33	59.37	18.70			
E22	1.5	1.6	4.5	5.6	25.53	9.73	0.58	61.62	26.35	13.97	0.13	59.36	18.71					
B3-24	1.2	1.8	7.9	7.9	22	13.2	0.7	63.5	0.2	22.03	18.39	0.05	0.11	59.35	18.73			
B7	1.9	1.8	6.6	6.6	26.6	5.2	0.5	60.3	0.7	28.69	7.80	2.50	0.30	60.71	18.91			
BZ-1	1.7	4	6.6	3.6	0.68	0.17	0.92	59.4	3.872	1.02	0.08	59.54	19.19					
B3-29	0.9	0.9	21.44	12.96	19.7	13.2	0.4	63.66	21.50	18.08	0.82	59.59	19.19					
A2-9	0.9	1.9	4.7	4.7	18.9	9.8	0.3	62.5	0.6	23.90	14.11	1.41	0.23	60.36	19.30			
BZ-41	7.9	8.1	3.7	3.7	17.6	4.9	17.5	61.3	1	20.20	14.57	3.89	0.18	61.16	19.50			
BZ-428	1.4	3.3	3.2	2.0	20.2	9.8	0.2	62.6	0.3	21.20	14.31	3.06	0.12	61.32	19.59			
BZ-406	3	8.2	19.7	19.7	13.2	9.9	0.2	58.5	0.6	16.77	15.19	7.68	0.12	60.24	19.69			
BZ-26	2.7	1.8	31.08	5.25	0.05	61.33	0.6	32.49	7.64	0.03	59.85	19.69						
722	1.3	1.3	1.3	1.3	17.6	4.9	0.2	59.1	0.6	20.08	7.78	9.09	0.13	62.93	19.72			
BZ-51	0.4	5.7	4.4	4.4	28.13	7.54	0.1	61.83	0.6	29.18	10.88	0.06	0.06	59.88	19.75			
723	0.6	0.6	17.7	27.2	9.8	5.1	0.3	62.8	0.6	22.10	14.21	2.42	0.17	61.70	19.78			
BZ-39	6.3	7.8	18.3	20.9	9.8	5	0.4	62.4	0.6	21.94	14.31	2.39	0.23	61.13	19.88			
BZ-40	6.2	8.9	9	22.1	4.9	10.3	0.3	60.8	0.6	24.41	7.53	5.18	0.18	62.69	20.21			
BZ-5	1.4	6.2	4.3	15.1	18.1	0.3	0.1	66	0.2	14.78	24.65	0.13	0.05	60.31	20.69			
B16	1.7	1.5	1.7	1.7	16.1	9.7	13.2	0.3	60.3	0.6	17.49	14.66	6.53	0.18	61.14	20.87		
BZ-37	2	6.6	6.3	19.2	9.7	7.1	0.2	62.9	0.5	20.26	14.24	3.41	0.12	61.97	20.92			
BZ-412	2	3.2																

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

EP 0 710 628 A2

Table 2 ... (sheet 3)

Comp	wt%	Shrinkage	100°C	1200°C	1260°C	Composition	wt%	Al2O3	TiO2	SiO2	Others	CuO	MgO	ZnO	Al2O3	TiO2	SiO2	SiO2 excess	Diopsidic Wollastonite Ratio	Comments
BZ-40S	1.6	3.9	/ /	20.4	9.9	5.4	0.3	63.2	0.5	21.05	14.42	2.57	0.17	61.78	20.99					
BZ-3.4	1.53	13.3	31.64	0.67	0.41	5.91		59.54	0.5	34.35	1.02	0.20	3.55	50.68	21.16					
BZ-5.5	1.3	6.4	14.6	9.8	15.5	0.2		59	0.5	16.14	15.07	7.80	0.12	60.87	21.21					
BZ-4.3	4.4	4.9	19	9.7	7.7	0.3		63	0.4	20.06	14.25	3.41	0.17	62.10	21.29					
BZ-11	0.9	2.7	33.25	0.59	2.33	0.69		61.71	0.5	35.10	3.42	0.28	0.40	60.80	21.31					
BZ-4.5	0.8	2.7	5	19.3	4.8	13.7	0.4	61.3	0.6	21.59	7.47	6.67	0.25	64.02	21.37					
BZ-6	2.2	3.9	4.7	17.2	9.8	10.3	0.2	61.8	0.5	18.43	14.61	5.02	0.12	61.82	21.72					
BZ-3	0.6	0.8	27.2	22.3	4.9	0.3	0.4	6.6	0.3	23.74	2.26	0.15	0.23	4.93	63.69	32.17				
BZ-2	0.4	0.9	24.9	23.7	4.9	0.1	0.4	4.8	0.3	23.02	7.20	0.05	0.23	3.56	63.95	31.41				
BZ-7.2	0.5	19.6	19.2	4.9	6.7	0.3	3.6	61.3	0.4	20.92	7.43	3.32	0.18	2.75	65.40	30.22				
BZ-1	0.6	1.1	20	26.2	4.9	0.1	0.4	2.8	0.4	27.50	7.16	0.05	0.23	2.06	63.00	28.02				
D12	0.5	0.8	+8	13.7	10.4	5.5	0.1	2.7	0.3	14.33	15.13	2.52	0.06	1.98	63.98	33.95				
D11	0.6	0.9	8.6	14.4	11.1	5.3	0.1	2.7	66.4	0.3	14.97	16.06	2.51	0.06	1.97	64.44	30.85			
D10	1.1	1.3	4.6	15.7	11.7	4.9	0.1	2.7	64.7	0.3	16.26	16.86	2.31	0.06	1.96	62.55	27.06			
D5	0.6	0.8	5.2	14.3	11.7	5.4	0.1	2	66.4	0.4	14.82	16.87	2.55	0.06	1.46	64.25	29.95			
BZT-1	0.9	1.3	29.5	24.3	4.9	3.3	0.4	1.9	0.5	25.88	7.26	1.60	0.23	1.42	63.67	27.04				
D4	0.9	1.6	7.2	16.4	12.2	5.4	0.2	1.8	62.8	0.3	17.11	17.77	2.56	0.11	1.32	61.77	21.67			
KP-7		4.9	2.9	0.1	44.5	51.7	0.2	3.82	0.18	0.06	32.28	0.06	0.07	3.35	63.65	27.24				
BZ-6.4	18.8	21.6	24.83	4.59	0.15	5.7	63.24	0.2	26.57	6.83	0.06	0.07	3.35	63.17	26.26					
BZ-2.1	3.3	7.5	32.3	0.48	0.12	4.15		60.83	0.3	35.08	0.73	0.06	0.06	2.48	61.66	23.26				
BZ-3.4	4.3	7.4	25.47	4.68	0.38	3.97		63.74	0.2	27.07	6.94	0.28	0.28	2.33	63.39	26.49				
BZ-4.4A	1	1.4	11.4	25.81	4.88	0.24	2.03	65.5	0.2	27.18	7.15	0.12	1.19	64.37	28.63					
BZ-4.40E				16.9	6.5	5.8	1.7	0.1	68.4	0.4	18.09	9.68	2.83	1.00	0.06	68.33	33.92			
BZ-3.60F				11.4	9.5	1.5	0.1	61.7	0.5	12.76	14.17	7.64	0.92	0.08	64.44	28.96				
BZ-1.6				6	17.2	11.9	3.4	1.4	65.4	0.4	17.77	17.05	1.59	0.79	0.78	62.86	25.38			
BZ-3				3.9	12.6	12.4	0.6	1.4	65.8	0.3	18.92	17.55	0.28	0.78	0.78	62.47	24.67			
B6	1.1	1.1	2.9	3.5	19.2	14.2	0.1	0.2	66.1	0.4	19.05	19.60	0.05	0.11	0.11	61.20	22.41			
D7	0.7	1.1	2.2	2.7	18.5	13.5	1.7	0.2	65.1	0.2	18.57	18.85	0.78	0.11	0.70	60.99	22.68			
B10	1.6	1.6	2.6	3.2	16.8	15.9	0.3	0.2	67.1	0.2	16.49	21.71	0.13	0.11	0.07	61.48	23.04			
A2-10	1.9	2.2	2.2	3	16.22	15.8	0.49		66.17	0.1	16.18	21.93	0.27	0.27	0.27	61.62	23.24			
BZ-59	1	2.8	2.9	12.4	10	17.5	0.2	59.2	0.7	13.83	13.52	0.88	0.12	0.12	61.73	23.46				
BZD				12.6	18.3	13.8	0.8	0.2	63.5	1.3	18.45	19.36	0.37	0.11	0.07	61.64	23.28			
A2-5	1	1.9	1.9	18.74	13.78	0.14	0.18	65.69	0.1	18.85	19.29	0.06	0.10	0.10	61.69	23.39				
A2-31	1.9	2.3			8.45	21.72	0.64	0.32	67.62	0.2	8.26	29.33	0.28	0.17	0.17	61.73	23.46			
D1	1	1.7	7.2	16.3	12.5	5.6	0.1	63.3	0.3	16.96	18.10	2.63	0.06	0.13	61.50	23.72				
A2-8	1.5			16.86	14.24	1.17	0.22	65.33	1.7	20.15	20.15	0.54	0.12	0.12	62.03	24.06				
BZ-44	0.7	1.7	2.5	11	11.2	11	0.1	62.4	0.5	15.98	16.60	5.33	0.06	0.06	62.04	24.07				
A2-13	1.7	1.6	2.6	14.87	16.01	0.92	0.11	66.67	14.89	22.31	0.42	0.06	0.06	0.06	62.32	24.64				
BZ-40.4				5.7	16.4	12.6	5.3	0.1	64.6	0.7	16.95	18.12	2.49	0.06	0.07	62.31	24.70			
B7.4	6.7	18.3	13.7	0.3	0.2	0.1	0.1	66.8	0.6	18.29	19.03	0.6	0.07	0.07	62.33	24.74				

5

10

15

20

25

30

35

40

45

50

55

Table 2 .... (sheet 4)

Comp	Shrinkage				Composition				Composition				mole%				SiO <sub>2</sub> Excess	SiO <sub>2</sub> Dropside Wollastonite Ratio	Comments
	800°C	1000°C	1200°C	1260°C	CaO	MgO	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Others	SiO <sub>2</sub>	MgO	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>			
BZ-440C	1.8	16.2	12.6	5.3	0.1	0.1	0.1	0.1	0.1	16.82	18.21	2.51	0.06	0.07	6.23	24.74	0.65% Na <sub>2</sub> O	0.65% Na <sub>2</sub> O	
BZC	3.9	18	13.8	0.2	0.1	0.1	0.1	0.1	0.1	18.09	19.29	0.09	0.06	0.07	62.47	24.94	0.65% Na <sub>2</sub> O	0.65% Na <sub>2</sub> O	
BZ-4450C	4.9	15.5	11.9	7.5	0.1	0.1	0.1	0.1	0.1	16.27	17.38	3.58	0.06	0.07	62.63	25.33	0.65% Na <sub>2</sub> O	0.65% Na <sub>2</sub> O	
D8	1.5	1.4	1.6	1.9	1.8	0.4	1	0.1	0.1	16.2	17.11	0.83	0.22	0.71	62.54	25.80			
B19	1.1	1.5	1.6	1.9	1.6	0.7	0.1	0.1	0.1	16.87	17.11	0.1	13.65	22.95	0.31	0.05	0.07	62.97	26.00
BZ-4450H	0.8	1.5	2.1	12.4	9.9	15.8	0.2	0.1	0.1	16.08	16.82	3.40	0.64	0.07	62.99	26.06			
BZ-20	1.2	1.3	2.8	2.7	17.9	13.1	0.8	0.3	0.1	16.5	13.64	15.16	7.91	0.12	63.17	26.33			
B7	1	1.2	2.7	2.5	15.8	15	0.4	0.2	0.1	16.78	17.91	18.24	0.36	0.17	63.32	26.65			
B11	1	1.2	2.7	2.5	15.8	15	0.4	0.2	0.1	16.86	15.63	20.65	0.18	0.11	63.36	26.79			
BZ-4450I	0.7	1.4	2.3	2.1	15.9	12.1	5.2	0.2	0.1	16.43	16.77	16.83	3.45	0.72	63.40	26.87			
BZ-440	0.9	1.2	2.7	3.2	15.2	11.7	7.4	0.1	0.1	16.57	14.4	16.47	17.44	2.45	63.53	27.05			
BZ-4450	0.8	1.1	2.3	3.5	15.4	11.6	5.8	0.2	1	16.53	0.5	15.85	16.97	3.51	63.54	27.16			
D2	0.2	0.9	1.5	2	15	12.2	6.1	0.1	0.1	16.5	0.3	16.10	16.87	2.76	63.42	27.58			
BZ-437	0.2	0.9	1.5	2	15	12.2	6.1	0.1	0.1	16.57	0.3	15.60	17.66	2.89	63.79	27.59			
A2-33	0.3	1.4	1.7	1.9	10.5	9.9	17.6	0.1	0.1	16.04	0.1	16.4	17.44	2.45	63.45	27.86			
BZ-54	0.9	1.4	3.2	14.2	15.5	0.1	0.1	0.1	0.1	16.91	0.2	14.14	21.47	0.05	63.05	28.51			
B17	0.9	1.4	3.2	12.5	10	13.6	0.3	0.29	0.29	16.65	0.6	8.15	26.90	0.45	64.34	28.67			
A2-26	1.5	1.5	3.5	11.9	9	15.1	1	0.1	0.1	16.16	0.4	13.31	14.00	7.69	64.31	28.69			
BZ-560E	1	1	1.58	16.57	0.91	0.4	0.1	0.1	0.1	16.819	11.71	15.36	8.93	0.06	63.93	27.86			
A2-20	-	2.1	2.1	12.5	10	13.6	0.3	0.1	0.1	16.35	0.6	13.58	15.12	6.73	64.35	28.69			
RZ-58	0.2	1.1	1.7	17.45	12.6	0.98	0.19	0.1	0.1	16.833	0.7	17.67	17.75	0.18	64.40	28.80			
759	1.1	1.7	4.46	22.31	1.23	0.19	0.1	0.1	0.1	17.24	4.34	30.23	0.55	0.10	64.58	29.10			
A2-29	1.5	1.8	5.7	7/2	9/1	1.5/1	0.1	0.1	0.1	16.23	1.5	13.37	14.11	7.66	64.77	29.55			
BZ-560B	1.6	2.8	2	11.7	9.1	15.6	0.1	0.1	0.1	16.27	0.9	12.98	14.05	7.88	64.96	29.97			
BZ-560C	0.1	0.5	3.1	13.1	10.6	10.2	0.3	0.1	0.1	16.52	0.5	14.00	15.76	4.96	65.03	30.14			
BZ-560A	1.1	1.8	3.1	11.7	9.1	15	0.1	0.1	0.1	16.25	0.8	13.05	14.12	7.61	65.07	30.22			
BZ-560	1.1	1.1	3.1	15.9	12	1.87	0.1	0.9	0.9	16.29	0.5	13.01	13.92	7.64	65.06	30.65			
D9	1.1	0.5	2.2	10.4	9.8	15.7	0.1	0.1	0.1	16.82	0.2	16.26	17.07	8.87	65.05	30.84			
RZ-56	0.1	0.1	1.2	6.77	19.64	1.01	0.24	0.24	0.24	17.14	0.7	11.47	15.03	7.88	65.56	31.12			
A2-27	1.2	1.2	2	13.2	9.7	11	0.1	0.1	0.1	16.56	0.4	14.20	14.51	5.38	65.85	31.38			
BZ-61	0.2	1	2	15.17	12.76	1.13	0.07	0.07	0.07	16.29	1.546	18.09	0.52	0.04	65.89	31.79			
A2-6	1.5	0.8	3.8	13.6	11.3	5.7	0.1	0.1	0.1	16.73	0.3	14.24	16.46	2.72	65.79	32.31			
D3	0.3	0.4	1.7	8.1	9.7	18.2	0.1	0.1	0.1	16.31	0.4	9.12	15.19	9.32	66.30	32.61			
BZ-60	-0.1	0.4	1.7	8.1	9.7	18.2	0.1	0.1	0.1	16.70	0.7	27.03	0.45	0.13	66.79	33.59			
A2-32	1.1	1.1	1.1	11.58	14.52	1.38	0.15	0.15	0.15	17.03	1.178	20.55	0.12	0.08	66.86	33.72			
A2-17	1.1	1.1	9.36	16.34	0.83	0.33	0.33	0.33	0.33	17.48	9.42	22.88	0.38	0.18	67.14	34.28			
A2-22	1.1	1.1	2.4	13.1	9.8	8.6	0.1	0.1	0.1	17.4	0.4	13.99	14.56	4.18	67.20	34.41			
BZ-63	0.3	0.8	2.7	11.4	9.9	10.8	0.2	0.2	0.2	17.8	0.5	12.19	14.73	5.26	67.70	35.39			
BZ-8																			

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

EP 0 710 628 A2

Table 2 ... (sheet 5)

Comp	Shrinkage	Composition						Cation Mg/Al	Composition Mg/Al	Zr/Ti2	Al2O3/TiO2	SiO2/TiO2	SiO2/TiO2	Diopsidic Wollastonite Ratio	Comments		
		800°C	1000°C	1200°C	C.0	MgO	Zr/Ti2										
A2-15	1.1				12.67	12.35	1.24	0.11	72.23	12.94	17.55	0.58	0.06	68.88	37.75		
A2-16	0.7				12.4	10.09	2.21	0.19	73.43	12.90	14.61	1.06	0.11	71.32	42.65		
A2-28					2.07	17.15	1.70	0.15	78.07	2.08	23.93	0.80	0.08	73.10	46.20		
BZ-407	7	2.1			4.6	1.9	6.3	0.2	63.3	0.7	20.03	14.23	3.12	0.12	D		
BZ-429	0.7	1.8			4.1	17.8	9.7	0.2	62.4	1.1	19.07	14.46	3.95	0.12	(1) $\mu$ Vn2D		
BZ-19	0.7	1.1			2.2	17.4	5.1	0.3	60.8	0.6	19.68	8.02	7.93	0.19			
BZ-413	1.1	2.1			2.8	18.5	9.8	0.2	64.2	0.4	19.36	14.27	3.53	0.12	(1) $\mu$ Vn2D		
BZ-38	1.4	1.9			2.9	17.2	11.2	0.7	63.5	0.4	18.06	16.36	3.20	0.12			
BZ-53	1.1	2.8			2.3	3.3	14.5	1.0	13.3	0.1	61.2	0.5	15.82	15.18	6.60	0.06	(1) $\mu$ Vn2D
BZ-430	0.8	1.7			3.7	17	9.7	8.5	0.2	63.2	0.9	18.19	14.44	4.4	0.12		
BZ-418	0.6	1.1			3.3	18.4	9.1	6.6	0.2	64.8	0.4	19.44	13.37	3.17	0.12	(1) $\mu$ Vn2D	
BZ-414	0.3	1.4			1.7	1.9	17.3	9.9	0.2	65	0.4	18.34	14.43	3.53	0.12		
BZ-50	0.4	1.1			3.1	17.3	5	13.7	0.2	61.7	0.6	19.41	7.80	7.00	0.12	65.67	
BZ-62	0.6	1.8			2.3	15.4	9.9	10.7	0.1	62.9	0.9	16.59	14.84	5.25	0.06		
BZ-401	0.7	1.4			2.7	18.2	9.7	5.4	0.3	65.7	0.5	19.03	14.11	2.57	0.17	64.12	
BZ-435	0.3	1.4			1.5	16.6	11.3	5.3	0.6	64.9	0.7	17.36	16.44	2.52	0.35	63.34	
BZA-5					2.7	17.1	11.9	3.1	1	0.1	65.7	0.4	17.63	17.07	1.45	0.57	0.07
BZ-409	0.7	1			3	17.4	9.9	6.8	0.2	65.8	0.4	18.16	14.38	3.23	0.11	63.21	
BZ-431	1.2				2.6	16.1	9.8	8.6	0.2	63.9	0.6	17.24	14.60	4.19	0.12	64.11	
BZA-4					2.6	1.7	11.9	3.1	0.7	63.8	0.4	17.57	17.11	1.46	0.40	63.86	
BZ-46	0.3	0.7			1.2	1.8	14.9	4.9	17.3	0.3	61.2	0.7	17.13	7.85	9.06	0.19	63.47
BZ-403	0.5	1			2.4	17.4	10	5.8	0.2	66.1	0.4	18.17	14.53	2.76	0.11	63.75	
BZ-433	1.3	1.1			2.2	16.2	11.5	5.4	0.2	65.8	0.9	16.84	16.63	2.56	0.11	63.85	
BZ-400	0.6	1.3			2.3	17.1	9.7	5.4	0.2	66.6	0.4	17.94	14.16	2.58	0.12	65.21	
BZ-415	0.6	1.3			2.2	16	10	7	0.5	66.5	0.4	16.76	14.58	3.34	0.29	65.03	
BZ-410	0.6	1			1.6	16.4	9.8	6.6	0.1	66.8	0.4	17.18	14.28	3.15	0.06	65.33	
BZ-419	0.6	1.5			1.7	1.8	9.9	4.6	0.2	67.2	0.4	17.76	14.39	2.19	0.11	65.54	
BZ-36	0.5	0.7			1.3	16.5	5	12.6	0.2	64.9	0.6	18.36	7.74	6.38	0.12	67.40	
BZ-48	0.3	0.5			0.9	15.1	4.9	15.1	0.3	63.6	0.6	17.10	7.72	7.78	0.19	67.22	
BZ-4					1.6	16.2	9.7	5.7	0.5	67.4	0.5	16.97	14.13	2.72	0.29	65.89	
BZ-404	0.4	1.2			1.9	16.1	10	5.4	0.1	67.7	0.4	16.82	14.53	2.57	0.06	66.02	
BZ-52	0.3	0.5			0.6	13.4	5	17.5	0.2	62.8	0.6	15.39	7.99	9.15	0.13	67.34	
BZ-420	0.5	1.3			1.9	16.4	9.9	4.7	0.2	68.3	0.3	17.04	14.31	2.22	0.11	66.24	
BZ-44	0.7	1.1			2.4	14.8	9.6	7	0.3	67.3	0.4	15.69	14.16	3.38	0.17	66.60	
BZ-7	0.3				1.3	16.3	5	10.7	0.3	67.1	0.5	17.93	7.65	5.36	0.18	68.88	
BZ-426	0.2	1			2	16.3	9.8	3.6	0.2	69.4	0.3	16.90	14.13	1.70	0.11	67.16	
BZ-438	0.2	0.6			1.7	14.8	8.3	5.6	0.1	69.4	0.3	15.74	12.58	2.71	0.06	68.91	
BZ-35	0.2	0.9			1.7	18.1	5	12.2	0.2	63.2	0.3	20.18	7.75	6.19	0.12	68.76	
BZ-402	0.6	1.1			2.2	18.1	9.4	5.1	0.2	65.8	0.4	19.05	13.76	2.44	0.12	64.63	
BZ-425	0.7	1.1			2.2	17	9.7	3.4	0.2	68.5	0.3	17.69	14.04	1.61	0.11	65.54	

## EP 0 710 628 A2

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

Table 2 . . . (sheet 6)

Cmp	800°C	Shrinkage	1000°C	1200°C	1260°C	CaO	MgO	ZnO	Al2O3	TiO2	SiO2	Others	CuO	MgO	ZnO	Al2O3	TiO2	SiO2	SiO2 Excess	Diopside' Wollastonite Ratio	Comments
BZ-418	0.5	1.1	3.6	18.3	10	4.1	0.2	66.8	0.4	18.96	14.47	1.93	0.11	64.59	27.24	21.90					
BZ-416	1	0.9	4.7	19.3	9.8	5.2	0.2	64.7	0.4	20.15	14.23	2.47	0.11	63.04	23.61	20.69					
BZ-16	1.2	2.8	1.9	19.2	9.7	5.2	0.3	64.9	0.4	20.04	14.09	2.47	0.11	63.23	23.99	19.75					
BZ-42		2.6	2	3.1	19.3	9.7	0.1	66.4	0.3	18.82	17.27	0.28	0.56	63.07	25.86	18.86					
BZA-1	0.8	1.3	0.9	2	2.7	18.8	12.2	0.6	67.1	0.3	18.74	17.19	0.28	0.33	63.45	26.63	18.46				
BZ-160	0.2	1	0.9	2	2.4	18.4	9.9	0.2	64.8	0.4	20.14	14.08	2.42	0.17	64.11	23.88	16.60				
B4	0.9	1.5	1.9	1.9	1.9	1.6	0.2	66.8	0.7	19.08	17.22	0.32	0.11	63.27	26.21	15.80					
BZ-424		0.9	1.9	3.6	19.4	9.7	4.1	67.1	0.3	19.07	14.27	1.65	0.11	64.90	28.15	12.77					
BZ-29	0.7	1.1	5.4	19.1	9.8	3.4	0.2	64.8	0.6	19.96	7.67	5.12	0.35	66.70	28.29	9.73					
BZ-417	0.8	1.3	2.9	20.7	9.8	6	0.1	66.7	0.4	20.09	13.97	1.93	0.11	63.39	25.85	8.93					
BZ-423	0.2	1.3	1.5	1.5	1.5	1.5	0.2	66.9	0.4	19.71	14.07	1.64	0.11	64.46	27.27	8.38					
BZ-421		1.5	2.9	3.2	1.9	1.5	0.9	64.7	0.5	20.87	14.12	2.03	0.51	62.53	23.04	7.88					
BZ-17	0.7	1	1.1	1.1	1.1	1.1	0.4	63.8	0.6	21.00	7.69	5.23	0.24	65.83	26.43	7.17					
BZ-42	0.9	0.9	2.6	19.1	9.9	3	0.2	66.7	0.5	19.77	14.26	1.41	0.11	64.45	27.48	7.36					
BZ-422	0.9	1.8	10.4	20.2	9.8	5.6	0.2	63.3	0.4	20.93	14.12	1.70	0.11	63.14	24.58	6.14					
B13	0.6	7	1.1	2.3	12.3	6	0.2	65.6	0.3	21.28	17.10	0.27	0.11	61.17	22.14	5.85					
BZ-31	0.2	0.4	2.2	18.3	5.1	8.6	0.3	66.5	0.6	19.99	7.75	4.28	0.18	67.80	31.33	5.42	F				
BZ-30	0.6	1.7	5.7	20.2	9	10.3	0.4	63.7	0.6	22.14	7.62	5.14	0.24	64.86	24.58	5.22					
BZ-432	0.7	0.9	6	20	8	5.5	0.2	65.7	0.6	21.16	11.78	2.65	0.12	64.30	25.94	5.18					
BZ-430	1.4	1.4	20.7	21	8.3	5.6	0.3	63.5	0.5	22.25	12.24	2.70	0.12	63.81	22.92	4.82					
BZ-37	1.5	2.1	1.1	21.1	9.8	3.2	0.3	64.2	0.5	21.92	14.16	1.51	0.17	62.24	22.97	4.63					
B14	1	0.9	5	20.3	11.4	0.2	0/	67.1	0.2	20.51	16.02	0.1/	0.07	63.28	26.64	4.57					
BZ-33	0.3	0.7	4	20.3	5	8.2	0.3	65	0.6	22.11	7.58	4.06	0.18	66.07	28.08	3.45					
B18	1.1	1	12.2	22.8	10.2	0.5	0.3	64.8	0.2	23.28	14.49	0.23	0.17	61.76	23.36	2.80					
BZ-34	0.6	1.1	5	22.2	4.9	8.1	0.3	63.2	0.6	24.17	7.42	4.01	0.18	64.22	24.43	2.77					
B3-22	0.8	1.1	21.28	3.94	0.54	0.52	0.1	66.17	0.6	22.04	13.46	0.25	0.30	63.36	27.66	2.73					
B21	0.6	0.5	7.1	22.3	9.3	0.6	0.2	67.1	0.2	22.68	13.16	0.28	0.11	63.70	27.19	2.53					
B3-23	1	21.26	9.33	0.3	0.56	0.1	64.09	0.2	24.10	13.45	0.14	0.32	61.99	23.83	2.32						
B3-28	0.2	18.74	7.03	0.75	0.47	0.1	70.81	19.68	0.27	0.36	0.27	0.45	69.42	38.47	2.26						
B3-27	0.7	0.8	20.98	7	0.70	0.78	0.1	68.56	0.2	21.97	10.20	0.38	0.45	67.01	33.64	1.99					
BZ-35	1.2	1.3	9	24.1	5	5.2	0.3	63.8	0.6	25.88	7.47	2.54	0.18	63.99	25.34	1.94	G				
719	0.5			25.69	8.12			65.77		26.11	11.48			62.40	24.81	1.78					
718	0.4			27.14	6.95	0.49		65.23		27.72	9.87	0.23		62.18	24.13	1.59					
B3-14	0.6	0.3	24.91	5.54	0.61	0.58		65.11		26.50	8.20	0.30	0.34	64.66	29.03	1.50					
721	0.5	0.4	29.79	5.4	0.43	0.43		65.08		28.56	7.77	0.03		63.64	27.28	1.37					
723	0.5	0.4	23.7	3.76	0.47	0.43		62.61		31.10	7.90			61(W)	22.01	1.44					
B3-18	0.4	0.5	24.91	3.65	0.65	0.45		69.42		25.16	5.55	0.23		68.80	37.38	1.31					
B3-19	0.5	0.5	24.99	1.71	1.03	0.65		67.58		26.61	5.42	0.32		67.39	34.45	1.29					
B3-16	0.2	0.3	24.99	2.06	0.91	0.55		68.74		27.06	2.58	0.51		69.47	38.44	1.15					
B3-13	0.9	0.8	30.62	2.06	0.91	0.55		62.33		31.14	3.10	0.45		62.98	25.51						

5

10

15

20

25

30

35

40

45

50

55

Table 2 ... (sheet 7)

Comp	Shrinkage			Composition			Composition			Composition			Composition			Comments
	800°C	1000°C	1200°C	CuO	MgO	ZnO	Al2O3	TiO2	SiO2	CuO	MgO	ZnO	Al2O3	TiO2	SiO2	
B3-17	0.3	26.68	1.86	0.57	0.7	67.25	28.79	2.79	0.28	0.42	67.73	35.17	1.13			
B3-15	0.3	29.82	1.78	0.51	0.47	65.86	31.64	2.63	0.25	0.27	65.22	30.19	1.11			
E32		3.2	2	0.1	0.3	65.5	32.59	2.92	0.05	0.17	64.27	28.49	1.10			
B3-32	0.7	23.43	0.5	0.72	0.31	73.28	25.13	0.97	0.35	0.18	73.37	46.38	1.07			
B3-31	0.4	27.76	0.49	1.0	0.4	67.59	30.10	0.74	0.50	0.24	68.42	36.34	1.06			
E25	0.4	31.1	0.6	0.7	0.5	65.3	0.5	33.27	0.89	0.34	65.20	30.07	1.05			
E31	0.9	1.8	31	1	0.4	66.4	0.4	32.77	1.47	0.23	65.52	31.05	1.05			
E24	0.5	1.3	33	0.6	0.5	64.7	0.5	35.03	0.89	0.15	63.60	27.05	1.03			
E23	0.5	2.2	35.1	0.6	0.1	62.3	0.5	37.18	0.88	0.05	61.60	23.15	1.03			
B3-30	0.6	31.93	0.37	0.28	0.64	64.13	34.41	0.55	0.14	0.38	64.52	28.89	1.02			

EP 0 710 628 A2

Table 3 ... (sheet 1)

Comp	Lat	Composition		Wt%		Others		CuO	MgO	Composition		mol%		SiO2	MgO	SiO2	Total	MgO Excess	
		MgO	/Al2O3	Al2O3	TiO2	SiO2	TiO2			ZnO	Al2O3	TiO2	CuO	MgO					
KF-1	2.9	0.1	0.1	44.3	51.7	0.2	3.82	0.18	0.06	32.28	63.65	1.3	1.3	-32.16					
C-18-4	19.7	0.4	0.2	36.6	42.5	0.5	24.58	0.69	0.11	25.12	49.50	5	9	-24.54					
C-18-10	50.8			24.6	23.6		58.62			15.67	25.51			-15.67					
BZ-3-1	31.64	0.67	0.41	5.91	39.54		34.55	1.02	0.20	3.55	60.68	25	10	6.5	-2.74				
BZ-2-1	32.3	0.48	0.12	4.15	60.83		35.08	0.73	0.06	2.48	61.66	61	5	5.8	1.24	-4.81			
BZ-2-1	17.6	4.9	17.5	0.2	59.1	0.6	20.08	7.78	9.09	0.13	62.93	8	3	12	2.3	-4.43			
BZ-46	14.9	4.9	17.3	0.3	61.2	0.7	17.15	7.85	9.06	0.19	65.75	9	3	16	2.8	-1.41			
BZ-52	13.4	5	17.5	0.2	62.8	0.6	15.39	7.99	9.15	0.13	67.34	7	3	11	2.1	-1.28			
BZ-48	15.1	4.9	15.1	0.3	63.6	0.6	17.10	7.72	7.78	0.19	67.22	6	3	9	1.8	-0.25			
BZ-47	18.9	5	15.2	0.3	59	0.7	21.47	7.90	7.86	0.19	62.57	11	3	17	3.1	-0.14			
BZ-2-1	22.3	5	15.2	0.3	56.4	0.7	23.06	7.82	7.77	0.19	59.16	14	3	26	4.3	-0.14			
BZ-23	26.5	5	14.9	0.5	51.4	0.6	29.95	7.86	7.66	0.31	54.22	17	3	23	4.3	-0.11			
BZ-19	17.4	5.1	15.4	0.3	60.8	0.6	19.68	8.02	7.93	0.19	64.18	8	3	24	3.5	-0.09			
B3-31	27.76	0.49	1.01	0.4	67.59	0.7	30.10	0.74	0.50	0.24	68.42	50	4	112	1.66	0.00			
BZ-25	20.7	5.2	15.5	0.3	57.3	0.7	23.35	8.16	7.96	0.19	60.34	8	3	16	2.7	0.02			
B3-30	31.93	0.37	0.28	0.64	64.13		34.41	0.55	0.14	0.38	64.52	83	3	16.3	2.49	0.04			
BZ-27	23.8	5.7	14.8	0.4	53.9	0.7	27.00	8.05	7.64	0.25	57.07	14	3	25	4.2	0.16			
E25	31.1	0.6	0.7	0.5	65.3	0.5	33.27	0.89	0.34	0.29	65.20	50		86	1.36	0.26			
B3-29	36	0.68	0.17	0.92	59.4		38.72	1.02	0.08	0.54	59.63	29	5	201	2.35	0.39			
B3-32	23.43	0.65	0.72	0.31	73.28		25.13	0.97	0.35	0.18	73.37	X	X	X		0.44			
E24	33	0.6	0.3	0.5	64.7	0.5	35.08	0.89	0.15	0.29	63.60	57			1.15	1.72	0.45		
E23	35.1	0.6	0.1	0.5	62.3	0.5	37.18	0.88	0.05	0.29	61.60	61		137	1.98	0.54			
BZ-45	19.3	4.8	13.1	0.4	67.3	0.6	21.59	7.47	6.67	0.25	64.02	13	5	18	3.6	0.55			
E22	37.1	0.7	0.1	0.6	60.2	0.5	39.20	1.03	0.05	0.35	59.37	64			1.62	2.26	0.63		
E21	39.1	0.7	0.6	0.6	58.2	0.5	41.28	1.03	0.03	0.35	57.35	58			225	283	0.68		
BZ-50	17.3	5	13.7	0.2	62.7	0.6	19.41	7.80	7.00	0.12	65.67	13	5	17	3.5	0.69			
BZ-49	20.9	4.9	13.2	0.3	59.5	0.7	23.37	7.62	6.72	0.18	62.10	11	3	16	3.0	0.72			
708	42.79	0.77			55.22		44.85	1.12			54.03	31	2	193	2.26	1.12			
BZ-36	16.5	5	12.6	0.2	64.9	0.6	18.36	7.74	6.38	0.12	67.40	8	3	16	2.7	1.24			
E31	31	1	0.4	0.4	66.4	0.4	32.77	1.47	0.23	0.23	65.52				21	32	1.44		
BZ-35	18.1	5	12.2	0.2	63.2	0.5	20.18	7.75	6.19	0.12	65.76	8	3						
B3-16	24.99	1.71	1.03	0.65	68.74		27.06	2.58	0.51	0.39	69.47	72	0	132	2.14	1.68			
BZ-29	18.1	5	10.2	0.9	64.8	0.6	19.96	7.67	5.12	0.55	66.70	70	7	27	4.1	2.07			
B3-17	26.68	1.86	0.57	0.7	67.25		24.41	7.53			67.73	49	13	162	2.24	2.10			
B3-15	29.82	1.78	0.51	0.47	65.86		21.64	2.63	0.25	0.27	65.22	38	7	156	2.01	2.11			
BZ-7	16.3	5	10.7	0.3	67.1	0.5	17.93	7.65	5.36	0.18	68.88	11	7	21	3.9	2.11			
BZ-5	22.1	4.9	10.3	0.3	60.8	0.6	24.41	7.53	5.18	0.18	62.69	14	7	22	4.3	2.17			
BZ-17	19	5	10.4	0.4	63.8	0.6	21.00	7.69	5.23	0.24	65.83	14	3	28	4.5	2.21			
BZ-30	20.2	5	10.3	0.4	63.4	0.6	22.14	7.62	5.14	0.24	64.86	16	5	33	5.4	2.24			
BZ-11	26.2	5	10.2	0.4	57.4	0.8	28.60	7.59	5.07	0.24	58.49	25	7	33	6.5	2.29			

## EP 0 710 628 A2

Table 3. (sheet 2)

Comp.	Cat	Composition wt%						Composition mol%						Solubility			MgO Excess		
		MgO	Al2O3	TiO2	SiO2	Cat	MgO	ZrO2	Al2O3	TiO2	SiO2	CuO	MgO	SiO2	Total				
B3-13		30.62	2.06	0.91	0.55	62.33	33.14	3.10	0.45	0.33	62.98	41	7	151	199	2.33			
B2-13		22	5.1	10	0.5	50.9	35.00	7.76	4.98	0.30	51.96	38	12	42	92	2.48			
E32		31	2	0.1	0.3	65.5	0.7	32.59	2.92	0.05	64.27					2.70			
B3-11		31.25	2.13	0.59	0.69	61.71	35.10	3.42	0.28	0.40	60.80	28	15	162	205	2.74			
B3-9		14.49	2.5	0.49	0.76	60.28	36.35	3.67	0.24	0.44	59.31	8	5	175	188	2.99			
B3-21		36.82	2.43	0.08	0.73	57.38	38.96	3.60	0.04	0.43	56.98	23	6	173	216	3.13			
B2-34		22.2	4.9	8.1	0.3	63.2	24.17	2.42	4.01	0.18	64.22	35	13	26	74	3.23			
BZ-31		18.3	5.1	8.6	0.3	66.5	0.6	19.99	7.75	4.28	0.18	67.80	13	3	33	49	3.29		
BZ-33		20.3	5	8.2	0.3	65	0.6	22.11	7.58	4.06	0.18	66.07	34	13	33	82	3.33		
B3-64		24.83	4.59	0.15	5.7	65.24	26.57	6.83	0.07	3.35	63.17	7	26	59	3.47				
BZ-T-2		19.2	4.9	6.7	0.3	56	0.4	20.92	7.43	3.32	0.18	2.75	65.40	16	7	29	52	3.93	
B3-51		25.41	4.68	0.35	5.97	63.74	27.07	6.94	0.28	2.33	63.39	43	11	48	102	4.33			
BZ-9		31.8	5	5.1	0.6	56	0.6	33.95	7.43	2.46	0.35	55.80	63	30	133	226	4.60		
B3-1		32.56	4.8	0.82	0.79	60.11	34.36	5.58	0.39	0.46	59.21	84	17	146	217	4.73			
BZ-T-5		24.7	5	5.2	0.3	63.6	0.6	25.68	7.47	2.54	0.18	63.94	42	17	77	136	4.74		
B3-1A		32.27	3.99	0.09	1.74	60.32	31.92	5.84	0.04	1.01	59.19	54	51	149	254	4.79			
B3-19		24.91	3.65	0.45	0.45	67.58	26.61	5.42	0.32	0.26	67.39	44	21	163	228	4.84			
BZ-1		26.6	5.2	0.5	0.5	60.3	0.7	28.69	7.40	2.30	0.30	60.71	45	20	92	157	5.00		
B3-18		23.7	3.76	0.17	0.43	69.42	25.16	5.55	0.23	0.25	68.80	66	17	145	228	5.08			
BZT-1		24.3	4.9	3.3	0.4	1.9	64	0.5	25.88	7.26	1.60	0.23	1.42	63.67	44	13	68	125	5.43
B3-3		36.07	4.4	1.46	0.58	55.99	37.77	6.47	0.70	0.33	34.73	14	18	185	217	5.44			
BZ-560F		11.4	9.1	15	0.1	61.7	0.5	12.76	14.17	7.64	0.92	0.03	64.44					5.60	
396		35.03	3.9	0.13	0.13	58.65	36.77	5.69	0.08	0.08	57.46	54	19	182	235	5.62			
BZ-560E		11.9	9	15.1	1	61.6	0.4	13.31	14.00	7.69	0.62	0.08	64.31					5.70	
BZ-60		8.1	9.7	18.2	0.1	63.1	0.4	9.12	15.19	9.32	0.06	66.30	6	3	21	30	5.80		
B3-4A		25.81	4.88	0.24	2.05	65.5	27.18	7.15	0.12	1.19	64.37	52	16	82	150	5.85			
BZ-440F		16.9	6.5	5.8	1.7	68.4	0.4	18.09	9.68	2.83	1.00	0.08	68.33						
BZ-560C		11.7	9.1	15.6	0.1	62.7	0.9	12.98	14.05	7.88	0.06	0.08	64.95					5.85	
BZ-560		11.7	9	15.1	0.1	62.9	0.5	13.01	13.92	7.64	0.06	0.08	65.29	4	5	18	27	6.22	
660		34.65	4.83	1.75	0.06	57.74	36.13	7.01	0.66	0.66	56.20	69	23	132	247	6.35			
BZ-54		10.5	9.9	17.6	0.1	61.4	0.6	11.71	15.36	8.93	0.06	0.08	63.93	10	7	17	34	6.37	
BZ-560A		11.7	9.1	15	0.1	62.5	0.8	13.05	14.12	7.61	0.06	0.08	65.07					6.45	
BZ-560B		12	9.1	15.1	0.1	62.3	1.5	13.37	14.71	7.66	0.08	0.08	64.79					6.45	
BZ-59		12.4	10	12.5	0.2	59.2	0.7	13.83	15.52	8.88	0.12	0.12	61.64	8	7	23	38	6.51	
712		35.39	4.61	0.06	0.06	57.54	37.04	6.71	0.03	0.03	56.21	24	22	160	206	6.68			
BT-1		26.2	4.9	0.1	0.4	2.8	64.3	0.4	27.50	7.16	0.05	0.23	2.06	63.00	38	17	117	192	6.83
BT-3		22.3	4.9	0.3	0.4	6.6	0.1	0.3	23.74	7.26	0.13	0.23	4.93	63.69	45	19	116	180	6.88
BT-2		23.7	4.9	0.1	0.4	4.8	64.9	0.3	23.02	7.20	0.05	0.23	3.36	63.95	46	18	111	171	6.92
BZ-56		10.4	9.8	15.7	0.1	63.7	0.5	11.47	15.03	7.88	0.06	0.06	63.56	8	7	15	30	7.09	
BZ-20		12.4	9.9	15.8	0.2	61.5	0.5	13.64	15.16	7.91	0.12	0.12	63.17	7	7	27	41	7.12	

EP 0 710 628 A2

Table 3 ... (sheet 3)

Comp.	Cat.	Composition		wt%		SiO <sub>2</sub>	Others	CaO	MgO	Composition			molar	Solubility	CaO	MgO	SiO <sub>2</sub>	Total	MgO excess
		MgO	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>					Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>							
BZ-55	14.6	9.8	15.5	0.2		59	0.5	16.14	15.07	7.80	0.12		60.87	11	7	15	33	7.15	
BZ-22	17.1	9.8	15.2	0.4		56.7	0.7	18.83	15.02	7.62	0.24		58.29	13	9	27	49	7.15	
BZ-26	15.2	9.9	15.3	0.2		58	0.6	16.77	15.19	7.88	0.12		60.24	8	3	24	35	7.39	
BZ-28	19.4	9.9	15.1	0.3		54.5	0.6	21.30	15.12	7.55	0.18		55.85	13	7	25	45	7.40	
BZ-24	22.2	9.9	15	0.3		51.2	0.8	24.46	15.18	7.52	0.18		52.66	17	7	21	43	7.47	
B3-14	24.9	5.54	0.61	0.58		65.11	0.11	26.30	8.20	0.30	0.34		64.66	67	27	158	252	7.57	
692	34.34	5.44	0.17	0.13		59.82	0.08	35.08	7.71	0.08	0.07		57.04	67	23	140	230	7.58	
722	31.08	5.25	0.05	0.05		61.33	0.03	32.49	7.64	0.03	0.03		59.85	81	23	185	289	7.61	
721	27.26	5.33	0.06	0.06		65.08	0.03	28.56	7.77	0.03	0.03		63.64	68	20	153	241	7.73	
723	29.79	5.44	0.17	0.17		62.61	0.03	31.10	7.90	0.08	0.15		61.00	62	17	141	220	7.90	
BZ-57	16.1	9.7	13.2	0.5		60.3	0.6	17.49	14.66	6.55	0.18		67.4	11	7	15	33	7.95	
BZ-58	12.5	10	13.6	0.3		63.5	0.6	13.58	15.12	6.73	0.18		64.40	8	7	25	40	8.21	
B3-20	32.7	6.07	0.97	0.97		57.57	0.27	34.28	8.25	0.52	0.29		40	108	250	8.33			
694	33.1	6.02	0.17	0.27		58.39	0.5	34.41	8.71	0.18	0.15		56.65	66	27	133	226	8.47	
BZ-53	14.5	10	13.3	0.1		61.2	0.5	15.82	15.18	6.60	0.06		62.33	16	7	19	42	8.52	
696	30.91	6.15	0.24	0.21		58.81	0.12	32.68	9.05	0.12	0.12		58.04	48	37	163	248	8.81	
BZ-J3-2	20	8	5.5	0.2		65.1	0.6	21.16	11.78	2.65	0.12		64.30	37	16	48	95	9.07	
BZ-61	13.2	2.7	11	0.1		65.6	0.4	14.20	14.51	5.38	0.06		65.85	10	7	27	44	9.07	
BZ-12	21.3	9.7	10.2	0.3		57.8	0.8	22.77	14.42	4.96	0.18		57.67	22	13	34	69	9.29	
BZ-8	11.4	9.9	10.8	0.2		67.8	0.5	12.19	14.73	5.26	0.12		67.70	10	10	30	50	9.36	
B3-27	20.98	7	0.79	0.78		68.56	0.5	21.97	10.20	0.38	0.45		67.01	54	20	122	196	9.37	
BZ-6	17.2	9.8	10.3	0.2		67.8	0.5	18.43	14.67	5.02	0.12		61.82	14	10	27	51	9.47	
BZ-62	15.4	9.9	10.7	0.1		62.9	0.9	16.59	14.84	5.25	0.06		62.26	11	10	30	51	9.53	
BZ-J3-40	21	8.3	5.6	0.3		63.5	0.7	22.25	12.24	2.70	0.24		62.81	25	12	46	83	9.54	
BZ-14	27.1	9.9	10	0.4		51.2	0.7	29.00	14.74	4.87	0.24		31.15	42	32	58	132	9.63	
D3-28	18.74	7.03	0.75	0.47		70.81	0.5	19.68	10.27	0.36	0.27		69.42	49	31	108	188	9.64	
718	27.14	6.95	0.49	0.49		65.21	0.23	27.72	9.87	0.23	0.23		62.18	47	20	107	174	9.65	
BZ-48	14.8	8.5	5.6	0.1		69.4	0.3	15.74	12.58	2.71	0.06		68.91	17	13	30	60	9.81	
BZ-40	18.4	9.1	6.6	0.2		64.8	0.4	19.44	13.37	3.17	0.12		63.90	30	17	51	98	10.08	
BZ-430	17	9.7	8.5	0.2		63.2	0.9	18.19	14.44	4.14	0.12		63.12	21	13	29	63	10.18	
BZ-431	16.1	9.8	8.6	0.2		63.9	0.6	17.24	14.60	4.19	0.12		63.86	17	11	33	61	10.29	
BZ-43	13.1	9.8	8.6	0.1		67.4	0.4	13.99	14.56	4.18	0.06		67.20	11	10	37	58	10.32	
BZ-427	19.6	9.7	8.7	0.2		60.8	0.6	20.93	14.47	3.94	0.12		60.60	29	16	43	88	10.36	
BZ-429	17.8	9.7	8.7	0.2		62.4	1.1	19.07	14.46	3.95	0.12		62.40	17	12	29	58	10.39	
BZ-428	18.9	9.8	8	0.3		67.3	1	20.20	14.57	3.89	0.18		61.16	8	4	17	26	10.50	
BZ-44	14.8	9.6	7	0.3		67.3	0.4	15.69	14.16	3.38	0.17		66.60	19	13	39	71	10.61	
BZ-610	13.1	10.6	10.2	0.3	0.1	65.2	0.5	14.00	15.76	4.96	0.18		65.03	7	10	27	44	10.62	
BZ-413	18.5	9.8	7.4	0.2		64.2	0.4	19.36	14.27	3.53	0.12		62.72	25	14	45	84	10.63	
BZ-43	19	9.7	7.1	0.3		63	0.4	20.06	14.25	3.41	0.17		62.10	32	20	55	107	10.66	
BZ-442	19.2	9.7	7.1	0.2		62.9	0.5	20.26	14.24	3.41	0.12		61.97	27	16	49	92	10.72	

5

10

15

20

25

30

35

40

45

50

55

## EP 0 710 628 A2

Table 3 .. (sheet 4)

Comp.	CaO	Composition		wt%		MgO		Al2O3		SiO2		Others		Composition		mol%		Solubility		MgO		SiO2		Total		Excess			
		MgO	ZnO	ZnO	Al2O3	TiO2	SiO2	Others	CaO	MgO	ZnO	Al2O3	TiO2	SiO2	CaO	MgO	SiO2	CaO	MgO	SiO2	Total	Excess	Excess	Excess	Excess				
BZ-414	17.5	9.9	7.4	0.2	65	0.4	18.34	14.43	3.53	0.12	63.58	11	39	7.1	10.79														
725	28.13	7.54	0.1	61.83	0.4	29.18	10.88	0.06	59.88	76	35	186	297	10.83															
BZ-411	20.3	9.8	7.7	0.2	67.6	0.4	27.42	14.39	3.47	0.12	60.67	24	13	38	72	10.86													
BZ-415	16	10	7	0.5	66.5	0.4	16.76	14.58	3.34	0.29	65.03	21	13	42	80	10.99													
BZ-407	19	9.7	6.5	0.2	63.5	0.4	20.03	14.23	3.12	0.12	62.50	22	13	45	78	11.03													
BZ-409	17.4	9.9	6.8	0.2	65.8	0.4	18.16	14.38	3.23	0.11	64.11	20	13	38	72	11.08													
BZ-410	16.4	9.8	6.6	0.1	66.8	0.4	17.18	14.28	3.15	0.06	65.33	21	13	27	49	11.21													
BZ-4	16.2	9.7	5.7	0.5	67.4	0.5	16.97	14.13	2.72	0.29	65.89	21	13	47	81	11.13													
BZ-406	20.2	9.8	6.4	0.2	62.6	0.3	21.20	14.37	3.06	0.12	61.32	33	20	67	119	11.14													
BZ-402	18.1	9.4	5.1	0.2	65.8	0.4	19.05	13.76	2.44	0.12	64.63	32	20	60	112	11.20													
BZ-411	15	11.2	11	0.1	62.4	0.5	15.98	16.60	5.33	0.06	62.04	11	11	27	49	11.22													
BZ-2	21.7	9.6	5.2	0.5	67.9	0.5	22.73	13.99	2.48	0.29	60.52	33	23	69	129	11.22													
BZ-401	18.2	9.7	5.4	0.3	65.7	0.5	19.03	14.11	2.57	0.17	64.12	28	20	64	102	11.37													
BZ-16	19.2	9.7	5.2	0.3	64.9	0.4	20.04	14.69	2.47	0.17	63.23	30	22	60	112	11.44													
BZ-400	17.1	9.7	5.4	0.2	66.6	0.4	17.94	14.16	2.58	0.12	65.21	30	22	61	113	11.46													
719	25.69	8.12	0.1	65.77	0.5	26.11	11.48	2.47	0.17	64.40	51	24	115	190	11.48														
BZ-160	19.3	9.7	5.1	0.3	64.8	0.4	20.14	14.08	2.42	0.17	63.11	26	19	50	95	11.49													
BZ-421	20.1	9.8	4.3	0.9	64.7	0.5	20.87	14.72	2.03	0.51	62.53	25	19	54	98	11.58													
BZ-39	21.2	9.8	5.1	0.3	62.8	0.6	22.10	14.21	2.42	0.17	61.10	39	43	68	190	11.62													
BZ-416	19.3	9.8	5.2	0.2	64.7	0.4	20.15	14.23	2.47	0.11	63.04	28	19	54	101	11.65													
BZ-403	17.4	10	5.8	0.2	66.1	0.4	16.17	14.53	2.76	0.11	64.43	31	19	60	110	11.66													
714	32	8.27	0.1	59.05	0.5	32.45	11.67	2.42	0.17	55.89	73	30	142	245	11.67														
BZ-405	20.1	9.9	5.4	0.3	63.2	0.5	21.05	14.42	2.57	0.17	61.78	44	25	78	147	11.68													
BZ-40	20.9	9.8	5	0.4	62.4	0.6	21.94	14.31	2.39	0.23	61.13	44	33	94	177	11.69													
BZ-404	16.1	10	5.4	0.1	67.7	0.4	16.82	14.53	2.57	0.06	66.02	35	20	67	122	11.91													
BZ-10	27.1	7.0	5	0.4	56	0.6	28.29	14.53	2.38	0.23	54.58	47	35	90	166	11.92													
BZ-417	19.4	9.7	4.1	0.2	66.1	0.4	20.09	13.97	1.93	0.11	63.89	28	19	56	103	11.93													
BZ-420	16.4	9.9	4.7	0.2	68.3	0.3	17.04	14.31	2.22	0.11	66.24	26	17	55	98	11.97													
BZ-419	17	9.9	4.6	0.2	67.2	0.4	17.76	14.39	2.19	0.11	65.54	22	16	39	77	12.09													
BZ-422	20.2	9.8	3.6	0.2	63.3	0.4	20.93	14.12	1.70	0.11	63.74	38	26	71	135	12.31													
BZ-423	19.1	9.8	3.5	0.2	66.9	0.4	19.71	14.07	1.64	0.11	64.46	33	25	72	130	12.31													
BZ-425	17	9.7	3.4	0.2	68.5	0.3	17.69	14.04	1.61	0.11	66.54	30	25	41	96	12.32													
BZ-426	16.3	9.8	3.6	0.2	69.4	0.3	16.90	14.13	1.70	0.11	67.16	29	23	56	108	12.32													
BZ-418	8.3	10	4	0.2	66.8	0.4	18.96	14.41	1.93	0.11	64.59	28	17	51	96	12.36													
BZ-41	23.1	9.8	3	0.4	62.5	0.6	23.90	14.11	1.47	0.23	60.36	47	47	122	226	12.47													
BZ-37	21.1	9.8	3.2	0.3	64.2	0.5	21.92	14.16	1.57	0.17	62.24	52	40	97	189	12.48													
BZ-424	18.4	9.9	3.5	0.2	67.1	0.3	19.07	14.27	1.65	0.11	64.90	28	22	51	101	12.51													
D12	13.7	10.4	5.1	0.1	2.7	0.7	67.6	0.3	14.33	15.13	2.52	0.06	1.98	22	19	43	84	12.55											
BZ-42	19.1	9.9	3	0.2	66.7	0.5	19.77	14.26	1.41	0.11	64.45	52	43	99	194	12.73													
B21	22.3	9.3	0.6	0.2	67.1	0.1	22.68	13.16	0.28	0.11	63.70	44	33	112	189	12.77													

## EP 0 710 628 A2

Table 3 (sheet 5)

Comp	Cat	Composition			wt%			Others	Cat	Composition			mol%			Solubility	Mgo	Site2	Total	Mgo	Excess
		Mgt	Zr(12)	Al(20)3	Ti(2)	Si(2)	Al(20)3	Ti(2)	Si(2)	Cu	Mgt	Zr(12)	Al(20)3	Ti(2)	Si(2)						
B2-4150B	15.3	11.5	7.1	7.1	0.1	64.2	0.4	16.08	16.82	3.40	0.64	0.07	62.99	12.79	29.1	12.90	57	17.4	29.1	12.90	
B3-22	21.28	9.34	0.54	0.52	66.17	22.04	13.46	0.25	0.30	63.96	62	3.1	13.3	21.4	12.98	48	3.1	13.3	21.4	12.98	
B3-25	28.15	9.22	0.48	0.46	59.53	29.08	13.25	0.27	57.40	57.40	48	3.1	10.1	17.6	12.99	44	3.1	10.1	17.6	12.99	
B3-23	23.26	9.33	0.3	0.56	64.09	24.10	13.45	0.14	0.32	61.90	44	3.1	10.1	17.6	12.99	44	3.1	10.1	17.6	12.99	
B2-38	17.2	11.2	6.7	0.2	63.5	0.4	18.06	16.36	3.20	0.12	62.25	40	3.2	60	13.05	13.05	13.05	13.05	13.05	13.05	
B3-26	30.5	9.44	0.62	0.62	56.98	31.39	13.52	0.35	54.74	54.74	64	4.1	14.9	25.4	13.17	64	4.1	14.9	25.4	13.17	
B2-4150.1	15.3	11.5	7.2	0.2	0.1	64.5	0.7	16.11	16.85	3.45	0.12	0.07	63.40	13.28	13.28	13.28	13.28	13.28	13.28	13.28	
B2-4150	15.2	11.7	7.4	0.1	0.1	65.3	0.5	15.85	16.97	3.51	0.06	0.07	63.54	13.40	13.40	13.40	13.40	13.40	13.40	13.40	
A2-16	12.4	10.09	2.23	0.19	73.43	12.90	14.61	1.06	0.11	71.32	45	5.5	11.3	21.3	13.44	21.3	5.5	11.3	21.3	13.44	
D1	14.4	11.1	5.3	0.7	27	66.4	0.3	14.97	16.06	2.51	0.06	1.97	64.44	13.49	13.49	13.49	13.49	13.49	13.49	13.49	
B2-435	16.6	11.3	5.3	0.6	64.9	0.7	17.36	16.44	2.52	0.35	63.34	29	3.0	68	13.57	13.57	13.57	13.57	13.57	13.57	
B3-24	25.3	9.73	0.58	0.62	61.62	26.35	13.97	0.33	59.36	37	5.7	18.5	27.9	13.64	27.9	5.7	18.5	27.9	13.64		
D3	13.6	11.3	5.7	0.7	67.3	0.3	14.24	16.46	2.72	0.06	0.74	65.79	13.69	13.69	13.69	13.69	13.69	13.69	13.69		
B2-4150C	15.5	11.9	7.5	0.7	0.1	63.9	0.8	16.27	17.38	3.58	0.06	0.07	62.63	13.74	13.74	13.74	13.74	13.74	13.74	13.74	
B2-433	16.2	11.5	5.4	0.2	65.8	0.9	16.84	16.63	2.56	0.11	63.85	26	2.0	55	13.96	13.96	13.96	13.96	13.96	13.96	
D2	15.4	11.6	5.8	0.2	1	65	0.3	16.10	16.87	2.76	0.11	0.73	63.42	14.00	14.00	14.00	14.00	14.00	14.00	14.00	
B18	22.8	10.2	0.5	0.3	0.1	64.8	0.2	23.28	14.49	0.23	0.17	0.07	61.76	14.09	14.09	14.09	14.09	14.09	14.09	14.09	
D5	14.3	11.7	5.4	0.7	2	66.4	0.4	14.82	16.87	2.55	0.06	1.46	64.25	14.27	14.27	14.27	14.27	14.27	14.27	14.27	
D10	15.7	11.7	4.9	0.7	27	64.7	0.3	16.26	16.86	2.31	0.06	1.96	62.55	14.49	14.49	14.49	14.49	14.49	14.49	14.49	
B2-437	15.	11.9	3.4	0.4	65.4	0.4	17.71	17.05	1.59	0.79	62.86	14	2.1	50	14.66	14.66	14.66	14.66	14.66	14.66	
BZ-440	15.9	12.1	6.1	0.1	65.7	0.3	15.60	17.66	2.89	0.06	0.79	63.79	14.71	14.71	14.71	14.71	14.71	14.71	14.71		
D4	16.4	12.2	5.4	0.2	1.8	62.3	0.3	17.11	17.71	2.56	0.11	1.32	61.17	15.03	15.03	15.03	15.03	15.03	15.03	15.03	
BZA-5	17.1	11.9	3.1	1	0.1	65.7	0.4	17.63	17.07	1.45	0.57	0.07	63.21	15.04	15.04	15.04	15.04	15.04	15.04	15.04	
B7A-4	17	11.9	3.1	0.7	65.8	0.4	17.57	17.11	1.46	0.40	0.34	63.47	15.25	15.25	15.25	15.25	15.25	15.25	15.25		
D1	16.3	12.5	5.6	0.7	1	63.3	0.3	16.96	18.10	2.65	0.06	0.73	61.50	15.39	15.39	15.39	15.39	15.39	15.39	15.39	
B2-440.1	16.4	12.6	5.3	0.7	0.1	64.6	0.7	16.95	18.12	2.49	0.06	0.07	62.31	15.57	15.57	15.57	15.57	15.57	15.57	15.57	
B2-440C	16.2	12.6	5.3	0.7	0.1	64.3	0.8	16.82	18.21	2.51	0.06	0.07	62.33	15.64	15.64	15.64	15.64	15.64	15.64	15.64	
B14	20.3	11.4	0.2	0.1	67.1	0.2	20.51	16.02	0.11	0.07	0.07	63.28	15.9	15.9	15.9	15.9	15.9	15.9	15.9		
D9	15.9	12	1.87	0.1	0.9	68.2	0.2	16.26	17.07	0.87	0.06	0.65	65.10	16.15	16.15	16.15	16.15	16.15	16.15	16.15	
A2-14	25.3	11.66	0.16	0.28	60.74	23.70	16.48	0.07	0.16	57.59	57	43	127	16.25	16.25	16.25	16.25	16.25	16.25	16.25	
BZA-2	18.5	12.2	0.6	1	66.4	0.3	18.82	17.27	0.28	0.56	63.07	24	6.6	115	16.43	16.43	16.43	16.43	16.43	16.43	16.43
BZA-3	18.6	12.4	0.6	1.4	65.8	0.3	18.92	17.55	0.28	0.78	62.47	24	6.1	109	16.49	16.49	16.49	16.49	16.49	16.49	16.49
BZA-1	18.5	12.2	0.6	0.6	67.1	0.3	18.74	17.19	0.28	0.33	63.45	25	6.9	119	16.58	16.58	16.58	16.58	16.58	16.58	16.58
A2-7	23.37	11.98	0.23	0.44	61.98	23.79	16.97	0.11	0.25	58.89	59	63	178	16.61	16.61	16.61	16.61	16.61	16.61	16.61	
B13	21.3	12.3	0.6	0.2	0.1	65.6	0.3	21.28	17.10	0.27	0.71	0.07	61.17	16.71	16.71	16.71	16.71	16.71	16.71	16.71	
B4	18.8	12.2	0.7	0.2	66.8	0.7	19.98	17.22	0.32	0.11	63.27	31	80	144	16.79	16.79	16.79	16.79	16.79	16.79	16.79
A2-15	12.67	12.35	1.24	0.11	72.25	12.94	17.55	0.58	0.06	68.88	35	48	105	16.91	16.91	16.91	16.91	16.91	16.91	16.91	
A2-9	21.41	12.96	1.49	0.36	63.66	21.30	18.08	0.82	0.82	59.59	66	195	328	17.26	17.26	17.26	17.26	17.26	17.26	17.26	
A2-6	15.17	12.76	1.13	0.07	69.29	15.46	18.09	0.52	0.52	65.89	48	70	152	17.52	17.52	17.52	17.52	17.52	17.52	17.52	

5

10

15

20

25

30

35

40

45

50

55

## EP 0 710 628 A2

Table 3 ....(sheet 6)

Comp.	Cat	Composition		wt%		Composition		mol%		Solubility		CaO	MgO	SiO <sub>2</sub>	Total	MgO Excess			
		MgO	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	(Others)	Cat	MgO	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Cat	MgO	SiO <sub>2</sub>	Total		
D8		16.9	13.2	7.8	0.4	7	66.2	0.2	17.1	18.59	0.83	0.22	0.71	62.54	33	39	66	140	17.54
B7		17.9	13.1	0.8	0.3		67.8	0.2	17.91	18.24	0.36	0.17		63.32	44	45	110	199	17.71
759		17.45	12.6				68.33	0.2	17.67	17.75	0.22	0.17		64.58	38	40	117	195	17.75
D7		18.5	13.5	1.7	0.2	1	65.1	0.2	18.57	18.85	0.78	0.11	0.70	60.99	34	36	63	133	17.96
A2-18		26.29	13.07	0.66	0.2		56.96	0.2	26.85	18.48	0.37	0.37		54.30	47	57	161	265	18.11
B12		22	13.2	0.7	0.2	0.1	63.5	0.2	22.03	18.39	0.05	0.11	0.07	59.35	45	43	106	194	18.23
A2-11		24.28	13.24	0.08	0.25		60.32		24.48	18.57	0.04	0.14		56.77	72	16	119	207	18.40
924		19.78	14.54	0.66	2.57		61.32	19.99	20.44	0.30	1.43		57.84	36	37	77	150	18.71	
B71		18.3	13.7	0.3	0.2	0.1	66.8	0.6	18.29	19.05	0.14	0.11	0.07	62.33					18.87
B7D		18.3	13.8	0.8	0.2	0.1	65.5	1.3	18.45	19.36	0.37	0.11	0.07	61.64					18.88
A2-5		18.74	13.78	0.14	0.18		65.69		18.85	19.29	0.06	0.10		61.69	48	60	150	258	19.12
B7C		18	13.8	0.2	0.1	0.1	66.6	0.7	18.09	19.29	0.69	0.06	0.06	62.47					19.15
B6		19.2	14.2	0.1	0.2	0.1	66.1	0.4	19.05	19.60	0.05	0.11		61.20	50	53	144	247	19.44
A2-8		16.86	14.24	1.17	0.22		65.33	17.15	20.15	0.54	0.12		62.03	54	84	181	319	19.49	
A2-17		11.58	14.52	1.58	0.15	0.15	70.43	11.78	20.55	0.73	0.08		66.80	35	72	91	198	19.73	
B11		15.8	15	0.4	0.2	0.1	68.6	0.2	15.63	20.65	0.18	0.11	0.07	63.36	32	45	101	178	20.36
B5		19.9	15.7	0.7	0.2	0.1	64.2	0.4	19.71	20.80	0.05	0.11	0.05	59.34	43	48	99	190	20.63
932		21.6	15.65	0.11	1.5		59.85	2.5	21.58	21.75	0.05	0.82		55.80	47	43	92	176	20.87
757		20.92	15.22	0.2	0.2	0.2	62.6	20.79	21.04	0.11	0.11		58.06	62	73	187	322	20.93	
B17		14.2	15.5	0.1	0.1	0.1	69.1	0.2	14.14	21.47	0.05	0.05	0.07	64.22	32	45	91	168	21.37
B10		16.8	15.9	0.3	0.2	0.1	67.1	0.2	16.49	21.71	0.13	0.11	0.07	61.48	30	43	95	168	21.47
A2-10		16.22	15.8	0.49	0.49		66.17	16.18	21.93	0.27	0.27		61.62	42	52	122	216	21.66	
A2-13		14.87	16.01	0.92	0.11	0.11	66.67	14.89	22.31	0.42	0.06		62.32	47	70	159	276	21.83	
A2-22		9.36	16.34	0.83	0.33		71.48	9.42	22.88	0.38	0.18		67.14	36	75	126	237	22.31	
734		26.62	17.05	0.05	/	0.1	56.58	25.66	22.87	0.02	0.53		50.92	52	66	135	253	22.32	
B19		13.9	16.8	0.7	0.7	0.1	68.7	0.1	13.65	22.95	0.31	0.05	0.07	62.97	29	49	174	192	22.58
A2-20		11.58	16.57	0.91	0.4		68.19	11.71	23.30	0.42	0.22		64.35	31	69	162	262	22.66	
973		24.45	16.81	0.05	0.5		56.18	24.31	23.25	0.02	0.27		52.14	42	47	102	191	22.96	
A2-28		2.07	17.15	1.76	0.15		78.07	2.08	21.93	0.80	0.08		73.10	X	X	X		23.05	
B9		18.1	17.1	0.1	0.2	0.1	64.4	0.2	17.72	23.39	0.04	0.11		58.84	32	44	101	177	23.14
971		23.92	17.36	0.05	0.74		56.82	23.56	23.79	0.02	0.40		52.23	55	31	69	162	23.36	
B8		18.8	17.9	0.3	0.2		63	0.2	18.30	24.24	0.13	0.11		57.23	30	39	90	159	24.00
B16		15.1	18.1	0.3	0.1	0.1	66	0.2	14.78	24.65	0.13	0.05	0.07	60.31	35	64	131	230	24.46
A2-12		16.55	18	0.05	0.33		63.56	16.37	24.76	0.02	0.18		58.67	47	66	160	273	24.56	
A2-30		16.06	18.21	0.4	0.4		63.68	15.89	25.07	0.22	0.22		58.82	33	52	102	187	24.85	
A2-23		18.59	18.78	0.05	0.48		60.2	18.37	25.82	0.02	0.26		55.53	47	92	192	274	25.53	
A2-26		8.12	19.26	0.98	0.29		68.65	8.15	26.90	0.45	0.16		64.34	31	97	183	311	26.29	
A2-32		6.36	19.6	0.36	0.23		73.09	6.23	26.70	0.16	0.12		66.79	X	X	X	64	26.41	
A2-27		6.77	19.64	1.01	0.24		71.14	6.70	27.03	0.45	0.13		65.69	24	67	101	192	26.44	
71		24.04	19.66	0.2			54.68	23.44	26.67	0.11			49.77	55	62	133	230	26.57	

Table 3 ... (sheet 7)

Comp.	Cat()	Composition				Mg(OH) <sub>2</sub>	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Others	Cat()	Composition				Mg(OH) <sub>2</sub>	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Cat()	Solubility				MgO Excess			
		Cat()	MgO	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Cat()	Mg(OH) <sub>2</sub>	ZnO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Cat()	MgO	SiO <sub>2</sub>	Total						Cat()	MgO	SiO <sub>2</sub>	Total				
A2-19		18.48	19.74	0.54	58.71	18.29	27.18	0.29	54.24	42	66	125	233	26.89																
A2-21		13.74	19.98	0.13	0.34	64.16	13.51	27.34	0.06	0.18	58.90	28	56	160	244	27.10														
A2-31		8.45	21.72	0.64	0.32	67.62	8.26	29.55	0.28	0.17	61.73	26	72	103	201	29.09														
A2-29		4.46	22.31	1.23	0.19	71.24	4.34	30.23	0.55	0.10	64.77	21	105	94	220	29.59														
A2-33		4.61	22.85	1.01	0.25	70.04	4.50	31.05	0.45	0.13	63.86	X	X	X	X	X	30.47													
A2-24		13.62	22.74	0.05	0.57	61.38	13.25	30.79	0.04	0.17	55.76	27	87	136	250	30.59														
A2-25		10.99	24.18	0.07	0.35	62.36	10.66	32.64	0.03	0.18	56.48	35	105	160	300	32.44														
A2-35		8.88	24.88	0.47	0.29	64.12	8.56	33.37	0.21	0.15	57.71	18	106	61	185	33.01														
A2-34		6.63	26.2	0.8	0.33	64.85	6.37	35.01	0.35	0.12	58.15	11	119	39	169	34.54														
		7.65	3.9	35.07	2.12	57.78	3.62	45.26	1.08	1.08	50.04	16	169	100	285	44.18														

## Claims

1. Use as a refractory fibre at temperatures of 1000°C or more for a period of 24 hours of an inorganic fibre for which

a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours and comprising CaO, SiO<sub>2</sub>, MgO, optionally ZrO<sub>2</sub>, optionally less than 0.75mol% Al<sub>2</sub>O<sub>3</sub>, any incidental impurities amounting to less than 2mol% in total, and in which

5 a) the SiO<sub>2</sub> excess (defined as the amount of SiO<sub>2</sub> calculated as remaining after the above named constituents are crystallised as silicates) exceeds 21.8mol%;

b) the amount of CaO is greater than the sum of the amount of MgO and twice the amount of ZrO<sub>2</sub>; and,

c) the calculated ratio of diopside to wollastonite does not lie in the range from more than that of fibre E32 to 5.25.

10 2. Use of a refractory fibre as claimed in claim 1 in which the incidental impurities include TiO<sub>2</sub> in an amount less than 1.25mol%, preferably less than 0.8mol%.

15 3. Use of a refractory fibre as claimed in claim 1 or claim 2 in which the incidental impurities include Na<sub>2</sub>O in an amount less than 1.0wt%, preferably less than 0.5wt%, more preferably less than 0.3wt%.

4. Use of a refractory fibre as claimed in any of claims 1 to 3 in which the incidental impurities include Fe<sub>2</sub>O<sub>3</sub> in an amount less than 1.0wt%, preferably less than 0.6wt%.

20 5. Use of a refractory fibre as claimed in any of claims 1 to 4 in which Al<sub>2</sub>O<sub>3</sub> is present in an amount less than 0.5mol%.

6. Use of a refractory fibre as claimed in any preceding claim and in which the fibre comprises approximately (in mol%):-

25 CaO 17.69-20.18

MgO 7.75-17.22

ZrO<sub>2</sub> 0.32-6.19

SiO<sub>2</sub> 63.11-66.54

30 7. Use of a refractory fibre as claimed in claim 6 and in which the fibre comprises approximately (in mol%):-

CaO 32.59-37.18

MgO 0.88-2.92

SiO<sub>2</sub> 61.6-65.52

35 8. Use as a refractory fibre as claimed in any of claims 1 to 7 and which is saline soluble.

9. Use as a saline soluble refractory fibre as claimed in claim 8 in which the excess MgO (defined as the amount of MgO less the sum of the amounts of ZrO<sub>2</sub> plus Al<sub>2</sub>O<sub>3</sub>) exceeds 10mol%.

40 10. Use as a saline soluble refractory fibre as claimed in claim 9 in which the excess MgO exceeds 11.3mol%.

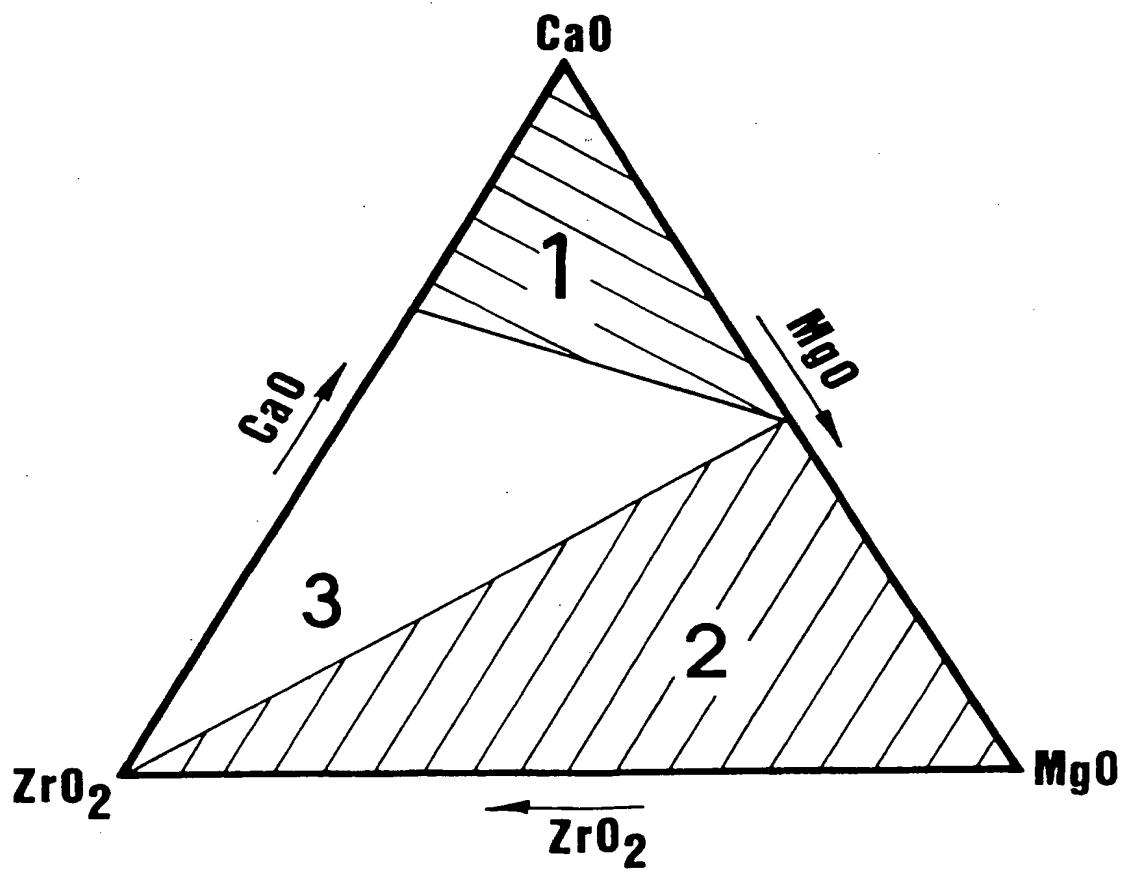
11. Use as a saline soluble refractory fibre as claimed in claim 10 in which the excess MgO exceeds 15.25mol%.

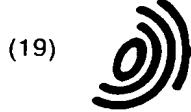
45

50

55

Fig.1





(19)

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 0 710 628 A3

(12)

## EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
29.05.1996 Bulletin 1996/22

(51) Int Cl. 6: C03C 13/00

(43) Date of publication A2:  
08.05.1996 Bulletin 1996/19

(21) Application number: 95120642.4

(22) Date of filing: 12.01.1994

(84) Designated Contracting States:  
AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL  
PT SE

(30) Priority: 15.01.1993 GB 9300085  
15.01.1993 MX 9300200  
09.07.1993 GB 9314236

(62) Application number of earlier application in  
accordance with Art. 76 EPC: 94904238.6

(71) Applicant: THE MORGAN CRUCIBLE COMPANY  
PLC  
Windsor, Berkshire SL4 1EP (GB)

(72) Inventor: Jubb, Gary Anthony  
Worcestershire DY13 OLS (GB)

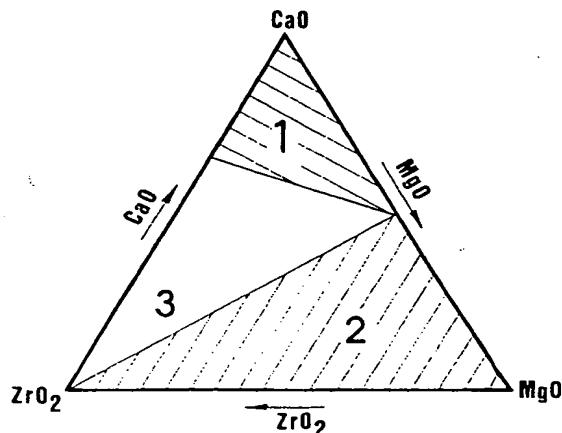
(74) Representative: Boff, James Charles et al  
c/o Phillips & Leigh  
7 Staple Inn  
Holborn  
London WC1V 7QF (GB)

## (54) Saline soluble inorganic fibres

(57) Use is disclosed, at temperatures of 1000°C or more for a period of 24 hours, of an inorganic fibre for which a vacuum cast preform of the fibre has a shrinkage of 3.5% or less when exposed to 1260°C for 24 hours and comprising CaO, SiO<sub>2</sub>, MgO, optionally ZrO<sub>2</sub>, optionally less than 0.75mol% Al<sub>2</sub>O<sub>3</sub>, any incidental impurities amounting to less than 2mol% in total, and in which

- the SiO<sub>2</sub> excess (defined as the amount of SiO<sub>2</sub> calculated as remaining after the above named constituents are crystallised as silicates) exceeds 21.8mol%;
- the amount of CaO is greater than the sum of the amount of MgO and twice the amount of ZrO<sub>2</sub>; and,
- the calculated ratio of diopside to wollastonite does not lie in the range from more than that of fibre E32 to 5.25.

Fig.1





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 95 12 0642

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.S)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
P,L, X	WO-A-93 15028 (THE MORGAN CRUCIBLE COMPANY PLC) * the whole document *	1-11	C03C13/00						
D,X	WO-A-87 05007 (MANVILLE CORPORATION) * claims 1-5 *	1-11							
D,X	WO-A-89 12032 (MANVILLE SALES CORPORATION) * claim 1 *	1-6,8-11							
X	WO-A-92 09536 (PAROC OY AB) * claim 1 *	1-5,8-11							
			TECHNICAL FIELDS SEARCHED (Int.Cl.S)						
			C03C						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>3 April 1996</td> <td>Reedijk, A</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	3 April 1996	Reedijk, A
Place of search	Date of completion of the search	Examiner							
THE HAGUE	3 April 1996	Reedijk, A							
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone      Y : particularly relevant if combined with another document of the same category      A : technological background      O : non-written disclosure      P : intermediate document</p> <p>T : theory or principle underlying the invention      E : earlier patent document, but published on, or after the filing date      D : document cited in the application      L : document cited for other reasons      &amp; : member of the same patent family, corresponding document</p>									